











# PHYSICAL CHEMISTRY

*A Co-operative Effort by a Group of Physical Chemists*  
*Third Edition — In Five Volumes*

EDITED BY

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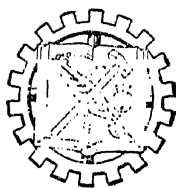
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## VOLUME TWO STATES OF MATTER

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## PREFACE

Some ten years ago, the publishers of this Treatise decided that the status of physical chemistry demanded an expansion of scope beyond the two volumes of preceding editions. A more ambitious enterprise involving the production of five volumes on the subject was planned. The cooperative feature of the effort was to be maintained. The subject was to be presented in a sequence of volumes, the first to contain an exposition of the fundamentals of Atomistics and Thermodynamics. This first volume was completed when war reached America and was published in March 1942. It was planned, prior to that time, to follow up the first volume "at intervals of several months by four volumes which should present in succession the States of Matter, Chemical Equilibrium, Chemical Kinetics and, finally, all those diverse elements that could be grouped under the title of Molecular Structure. The scope of the work was to be so broad that the student in a special field could garner from its pages that which was known as he set forth in his quest for the unknown."

That program and that schedule were casualties of World War II. Editorial activity and the collaboration of competent authors were lacking while the stresses of the war effort and of the post-war reconstruction years were with us. Indeed, authors who had been confidently relied upon to furnish the expanded effort were drawn away from fields of former interest to other more compelling activities. There have consequently been protracted delays in the construction of the work and an unevenness in the times of delivery of the finished chapters which has deprived some of the authors of rapid returns from their faithful labors. The renewed stresses of these last years have still further delayed the publication of this second volume which reviews our knowledge of the states of matter. Now it has become possible to present this material to include not only the kinetic theory of gases, the properties of both ideal and imperfect gaseous systems, the liquid state, and the solid state of aggregation as ascertained by X-ray analysis, but also the properties of matter in the colloidal state.

Over the years there have been anxious enquiries concerning and requests for the renewal of the effort. The editors and the publishers join in the hope that, with the publication of the present volume, the task of presenting the science of physical chemistry can now go forward less interruptedly so that the student of the science may once more possess "the accumulated experience of his predecessors" to enable him the better "to go forward to the new fields as yet unexplored." To all who have assisted in this undertaking the editor takes this opportunity to express his gratitude and indebtedness.

HUGH S. TAYLOR

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# CHAPTER I

## THE KINETIC THEORY OF IDEAL GASES

BY KARL F. HERZFELD

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A general outline of the atomic concept has been given in Volume I. The usefulness of this concept is greatly increased if it is combined with the kinetic theory. Pure thermodynamics needs no particular theory about the nature of heat, apart from the results implied in the first law, that heat is some kind of energy. The kinetic theory of heat, however, asserts that this energy is not a new type, but is entirely made up of the "hidden" motions of the particles (atoms and molecules) and a potential energy of elastic or electric kind connected with deviations from equilibrium positions, deviations which are due to the motion mentioned above. The motions are "hidden," in general, only on account of the small size of the particles, together with the irregularity of the motion, in the same way in which a crowd of people moving irregularly in different directions (without preference) seems at rest if seen from far above. The importance of the irregularity of the motions together with the importance of the large number of individuals is thus evident at the outset. These two characteristics will require a particular kind of mathematics, namely, the calculus of probability.

To explain, then, the general laws of thermodynamics, which apply to all substances, it is necessary to have a very general theory. This theory is treated in the subject of "statistical mechanics," but is not yet far enough developed to give everything in detail. In the case of the simplest substances, the gases, however, it is possible for the kinetic theory to give all the details.

This theory employs a method which is as essential here as in the other branches of theoretical physics. That is, as large a part of the theory as possible is built up from a greatly simplified model. To give an example, it is known, as explained in the first chapter, that in reality a molecule is a very intricate structure of electrons and nuclei moving in a complicated manner. In the case of many characteristic features of the behavior of the molecule, as in a rather rough description of its motion as a whole, this internal structure plays no rôle. Accordingly, in describing this motion the internal structure is disregarded and the molecule is treated as a hard solid sphere. This implies that the internal structure of the molecule does not affect its behavior as a whole. When the molecules are close together (dense gas), however, the details of their surfaces, their mutual forces, etc., become important, and it is then necessary to replace the primitive picture with one closer to reality, but much more complicated.



The kinetic theory of gases endeavors, then, to explain the behavior of a gas, not only as far as it is prescribed by the general thermodynamical laws, but also in so far as it is peculiar to a gas, with the simplest possible assumptions.

Comparison of a gas with a crystal shows as the most marked difference, that, in the latter case, there are internal stresses resisting both tension and compression, so that the crystal takes on a definite shape and volume, if constraints are absent, while a gas resists compression, but fills voluntarily and completely a volume of any size. Accordingly, it is natural to assume that there are in a crystal forces which tend to keep the molecules in a position of equilibrium, while in a gas at least the attractive forces are not sufficient to keep the molecules together. The simplest assumption, which will be made first, is that the forces between the gas molecules can be neglected entirely; the pressure exerted on the walls must then be explained as a kinetic effect, resulting from the impact of the gas molecules against this wall. The gas molecules move, according to this hypothesis, on the whole in straight lines (in the absence of an external force like gravity), which are occasionally broken by collisions among themselves or with the walls, during which collisions the molecules behave approximately like hard elastic spheres. The apparent uniformity of the gas density is only an average effect, due to the large number and swift irregular motion of the particles.

While a surprisingly correct theory of the forces in crystals was given as early as 1760 by Boscovich<sup>1</sup> and taken up in the elastic theories of Laplace, Navier, Poisson and Cauchy, the recognition that the gas pressure is entirely due to the dynamic effect of impacts took a long time. It is true that Bernoulli and Herapath<sup>2</sup> had expressed this opinion but one often finds, in papers from the first half of the nineteenth century, the expression "the elastic tension of gases." Waterstone in 1845 sent a paper to the Royal Society in which a large number of later developments were contained, but it was not deemed worthy of publication, and was only rediscovered and published by Lord Rayleigh in 1892. Following a new (1851) suggestion of Joule, the present theory of gases dates back to two papers by Krönig and Clausius.<sup>3</sup> Its brilliant development in the next 20 years is most closely connected with the names of Clausius, Maxwell and Boltzmann. Later contributions of importance will be found in the text.<sup>4</sup>

<sup>1</sup> *Theoria philosophiae naturalis redacta ad unicam legem virium in natura existentium* auctore Patre R. J. Boscovich, S. J., Venice (1758).

<sup>2</sup> D. Bernoulli, *Hydrodynamica* (Argentoratum, 1738); W. Herapath, *Phil. Mag.*, 62 (1823); 64 (1824).

<sup>3</sup> A. Krönig, *Pogg. Ann.*, 99, 322 (1856); R. Clausius, *ibid.*, 100, 366 (1857).

<sup>4</sup> The classical textbooks on the Kinetic Theory of Gases are: L. Boltzmann, *Vorlesungen über Gastheorie* (1st ed., Leipzig: 1898, 2 vol., 3d reprint, 1920); J. H. Jeans, *Dynamical Theory of Gases* (4th ed., Cambridge: 1925). Newer Books are: L. Bloch, *The Kinetic Theory of Gases* (London: 1924); L. B. Loeb, *Kinetic Theory of Gases* (2d ed., New York: 1934); R. C. Tolman, *Statistical Mechanics* (New York: 1927); G. Jäger, *Kinetic Theory* in Volume IX, *Handbuch d. Physik* (Berlin, 1926). The most complete modern English textbook is E. H. Kennard, *Kinetic Theory of Gases* (New York, 1938). For the exposition of the logical foundations of

The following symbols are used in this chapter:

$a, b$ van der Waals constants	$N$ number of molecules in vol. $v$
$c$ concentration (moles/cm <sup>3</sup> )	$R$ radius, gas constant per mole
$d$ diameter	$[R]$ Reynolds number
$e$ base nat. log.	$T$ °K
$f$ function, accommodation coefficient	$V$ molar volume
$g$ acceleration of gravity	$W$ bulk velocity
$k$ Boltzmann constant	$X, Y, Z$ coordinate axes
$k_t$ thermal diffusion constant	$Z$ = number of collisions
$l$ length	$N_A$ = Avogadro number
$m$ mass of molecule	$N$ = number of molecules/cc.
$n$ number of moles	$\alpha, \beta$ constants
$p$ pressure	$\delta$ thickness
$p_{12}$ shearing stress	$\epsilon$ energy per molecule ( $\epsilon_p$ = potential energy)
$r$ radius	$\eta$ viscosity
$t$ degrees Centigrade; time	$\vartheta$ colatitude
$v$ arbitrary volume	$\lambda$ thermal conductivity
$w$ molecular velocity	$\nu$ frequency
$\bar{w}$ relative velocity	$\rho$ density (mass)
$x, y, z$ position coordinates	$\sigma$ density of statepoints on surface of sphere
$\bar{m}$ effective mass = $\frac{m_1 m_2}{m_1 + m_2}$	$\tau$ time
$A$ area; constant	$\omega$ solid angle; angular velocity; element of volume in velocity space
$E$ energy per mole	$\varphi$ longitude
$F$ force	$\xi, \eta, \zeta$ components of $w$
$I$ moment of inertia	$\Delta$ mean free path
$M$ molecular weight, linear momentum per sec.; total mass	

## GASES IN EQUILIBRIUM

(1) **Gaseous Pressure. Boyle's Law:** Figure 1 shows a section of a rectangular box with sides of lengths  $l_1, l_2$ , and  $l_3$ . The box is fitted with a frictionless piston,  $A$ , which can move along the sides of length  $l_1$ . The walls of the box, together with the piston, are supposed to be perfectly smooth and elastic. The box contains a single molecule which is assumed to be a small, hard, perfectly elastic sphere. It is further assumed, for the present, that the molecule moves exactly parallel to the  $l_1$  edge as shown in Fig. 1. The influence of external forces such as gravity will be disregarded. Now the molecule will collide periodically with the piston and these impacts will set the piston in motion. To counteract this a force  $F$ , directed inward, is applied to the piston. That the piston will not be absolutely stationary is evident from the fact that the applied force is acting during the intervals between collisions and is then moving the piston into the box. At the instant of collision the impact prevails and the piston is driven in the reverse direction. The applied force must be of such magnitude that the two displacements are equal and opposite. This is the case if the applied force equals the time average of the impulsive forces

the theory and of many defects in the usual proofs see: P. and T. Ehrenfest, *Statistische Mechanik*, in Volume IV, 32, of *Enzyklopadie d. Math. Wiss.* (Leipzig, 1911).

of collision, which is the momentum imparted per second by the molecule to the piston.  $F$  is then equal to the "pressure" exerted by the molecule times the area of the piston.

The change of momentum accompanying each collision will first be calculated. A molecule of mass  $m$  and velocity  $\xi$  has a momentum equal to  $m\xi$ .

This is all imparted to the piston when the molecule is brought to a complete stop. Since however, both the piston and the molecule are perfectly elastic, they do not remain in contact,<sup>5</sup> but the molecule rebounds with its original speed. During this acceleration (which is similar to that experienced by a rubber ball when pressed against a hard plane and then released) a further momentum  $m\xi$  is given to the piston. From each collision, therefore, the piston receives a momentum directed outward and equal to  $2m\xi$ . Since the distance between the piston and the opposite wall is  $l_1$ , the time between two successive collisions is  $2l_1/\xi$ . Hence the number of collisions the molecule makes with the piston in unit time is  $\xi/2l_1$  and the total momentum received by the piston in unit time is

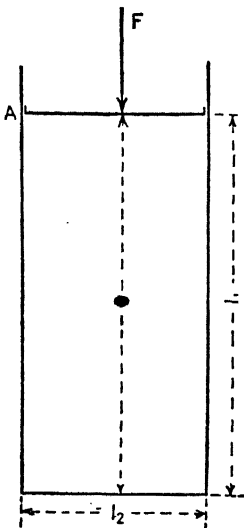


FIG. 1.

$$2m\xi \frac{\xi}{2l_1} = \frac{m\xi^2}{l_1} \quad (1.1)$$

which, at equilibrium, must be equal to the applied force.

If, instead of a single molecule, there are  $N_1$  molecules moving independently of each other but all exactly parallel to the  $l_1$  edge,  $N_1$  times as many collisions occur and the force is  $N_1$  times as great. The pressure (force per unit area) which is acting on the piston is therefore

$$p = \frac{N_1 \frac{m\xi^2}{l_1}}{l_2 l_3} = \frac{N_1 m \xi^2}{l_1 l_2 l_3} = \frac{N_1 m \xi^2}{v} \quad (1.2)$$

where  $v = l_1 l_2 l_3$ , the total volume of the box.

Since  $N_1 m$  is the total mass of the gas ( $M_1$ ) and  $M_1 \xi^2/2$  the kinetic energy of its molecules is  $E_{1k}(N_1/N_A)$ , then

$$pv = 2E_{1k} \frac{N_1}{N_A} \quad (1.3)$$

where  $E_{1k}$  is the kinetic energy of one mole of the molecules of type 1 and  $N_A$  is the Avogadro number.

<sup>5</sup> Actually they remain in contact for a short time, but this does not alter the result.

Actually the molecules do not move along exactly parallel paths <sup>6</sup> but, as will be seen in the following paragraphs, in all possible directions. This chaotic condition can be approximated by the assumption that one third of the total number of molecules  $N$  move up and down, one third from right to left, and one third backwards and forwards. Then

$$N_1 = \frac{1}{3}N \quad (1.4)$$

and (1.3) takes the form <sup>7</sup>

$$pv = \frac{2}{3} E_k \frac{N}{N_A} \quad (1.5)$$

$$\frac{N}{N_A} E_k = \frac{Nmw^2}{2} \quad (1.6)$$

where  $E_k$  is now the kinetic energy of one mole. That is, only one third of the total kinetic energy contributes to the pressure against a given wall.

If there are different kinds of molecules present, as in a mixture of gases, the argument remains unaltered and there is obtained

$$pv = \frac{2}{3} \left( E_k' \frac{N_1}{N_A} + E_k'' \frac{N_2}{N_A} + \dots \right) \quad (1.7)$$

where

is the total kinetic energy of all molecules of the  $s$ th kind.

Boyle's law is therefore a direct result of this assumption since the number of collisions in unit time, and therefore the pressure, is proportional to the density ( $N/v$ ) of the gas. In this discussion, it is assumed that the momentum imparted by each collision and hence the kinetic energy of the molecules is not dependent upon the volume, but upon other independent variables. This assumption will be proved in Section 5.

Upon increasing the number of molecules the time between two successive impacts is naturally decreased, at the same time diminishing the oscillation of the piston. It will be shown later on that under ordinary conditions (atmospheric pressure and room temperature) there are from  $10^{23}$  to  $10^{24}$  collisions per second on each square centimeter of the wall. The duration of each collision must be regarded as of much higher order of magnitude than the time between two successive collisions and in this case the effect may be correctly considered as a continuous pressure. The smaller the surface or the number of molecules, the smaller will be the number of collisions and the larger the relative irregularities of the state.

<sup>6</sup> Such an imaginary gas, all of whose molecules move parallel to each other is called a "one-dimensional gas." If the molecules are imagined to be moving in a plane, the result is a so-called two-dimensional gas.

<sup>7</sup> It should be noted that  $w^2 = \xi^2 + \eta^2 + \zeta^2$  where  $\xi$ ,  $\eta$  and  $\zeta$  are the components of the velocity  $w$ , along the  $X$ ,  $Y$  and  $Z$  axes, respectively.

The total pressure of a dilute gas is accordingly produced by the thermal motion of the molecules and is therefore known as a thermal pressure.

(2) **General Discussion of Averages. Uniform Distribution of Directions of Velocities:** In the preceding discussion it was seen that the pressure of a gas is determined by averaging over a large number of collisions. Similar considerations will frequently be used in the following pages. The next application will be to the directions of the velocities of the molecules, for the provisional assumption that the molecules could be divided into three equal groups, each moving parallel to a side of the box, was obviously only an approximation. Returning to the picture of a one-dimensional gas composed of molecules always moving parallel to a given edge of the box it is apparent that these molecules will not collide with each other. This state, however, is unstable since a small disturbance will cause a single molecule to move at an angle to the others and sooner or later collide with them, forcing them out of the original path. Thus, the original motion in a single direction will quickly change to one in which all directions appear in a uniform distribution. It may be assumed that in an ordinary gas, all directions of velocity appear equally often. For the justification of this assumption, it may be stated that, in the absence of external forces, there is no reason for the favoring of any special direction. It will be seen shortly that the shape of the containing vessel does not invalidate

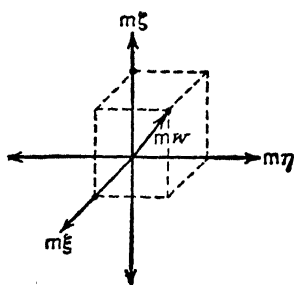


FIG. 2.

the last statement. Until then the container will be assumed to be a sphere. The situation may be represented by the following construction. Consider an ordinary system of rectangular coordinates (Fig. 2) and a single molecule with components of velocity  $\xi$ ,  $\eta$ ,  $\zeta$ , and, accordingly, components of momentum,  $m\xi$ ,  $m\eta$ ,  $m\zeta$ . The momentum of the molecule may be represented in this system of axes by the point  $m\xi$ ,  $m\eta$ ,  $m\zeta$ . Conversely, the position of the point uniquely determines the components of momentum and therefore the velocity. If the origin is connected to this "statepoint" the radius vector has the direction of the momentum (and velocity) of the molecule. This construction is to be carried out for all the molecules of the gas under consideration. The end points of these momentum vectors then give an exact picture of the directions of the momenta of all the molecules. Since the molecular velocities are supposed, for the present, to be of equal magnitude, all the end-points will lie on a sphere of radius

$$m\sqrt{\xi^2 + \eta^2 + \zeta^2} = m|w| \quad (2.1)$$

where  $|w|$  is the magnitude of the common velocity.

If the velocities are distributed uniformly over all directions, the points will lie on the sphere with uniform density (an isotropic distribution). If the

## THE KINETIC THEORY OF IDEAL GASES

points are represented by black dots upon a white ground, the surface of the sphere will appear uniformly gray. The "number of molecules moving in a definite direction" has no meaning since a definite direction corresponds to a single point on the sphere and it cannot be expected that one of the black dots, representing the endpoint of a momentum vector, will *exactly* coincide with this single point. Rather must the question be worded so that a definite latitude is allowed for the variation of the direction, that is, the given direction must be surrounded with an element of solid angle<sup>1</sup>  $d\omega$ . In the present representation this means the evaluation of the number of endpoints lying in a small area circumscribed about the given point. This evaluation has a meaning only when the whole area can be regarded as uniformly gray. In other words, the elementary area must contain a large number of dots. If the area is too small the exact position of its boundary becomes of importance and small changes in shape without appreciable changes in size will cause a *relatively* large change in the color content (number of included end points) since another dot may be taken into or excluded from the area (Fig. 3).

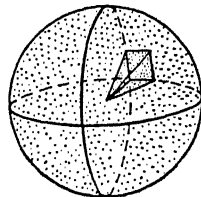


FIG. 3.

Such elementary areas and, in general, all magnitudes whose definitions require similar limitations are called "physically infinitely small."

If the density of the points on the surface of the sphere is designated by  $\sigma$ ,

$$N = \int \sigma d\omega \quad (2.2)$$

since all the molecules must be represented somewhere on the sphere.

The fraction of the total number of molecules whose representative points lie within a given elementary area  $d\omega$ , is

$$\frac{dN}{N} = \frac{\sigma d\omega}{\int \sigma d\omega} \quad (2.3)$$

In the case of the isotropic distribution the density,  $\sigma$ , is constant; hence,

$$\frac{dN}{N} = \frac{d\omega}{\int d\omega} = \frac{d\omega}{4\pi} \quad (2.4)$$

is the fraction of the total number of molecules present whose velocities have directions included in the elementary solid angle  $d\omega$  circumscribed about a given direction.

Instead of observing at a single instant all the molecules of a gas (space average) a single molecule may be followed for a long period of time. For example, the direction of its velocity may be recorded at a definite instant and at succeeding intervals of 0.001 sec. The different directions of motion of the same molecule so obtained may be plotted exactly as in the former case in

<sup>1</sup> It is not necessary that this elementary cone have a circular cross section.

which the velocities of different molecules were recorded simultaneously. In this case the sequence of the individual velocity vectors is of no importance, just as in the former case the relative position of the individual molecules did not come into consideration. Using this method there is obtained a picture identical with the former, containing more or less points corresponding to the number of observations taken. Thus, if there are too few molecules to give a sufficiently uniform coloring to the surface of the sphere, the usual space average may be replaced with a "time average" in which velocities to be compared are observed over a period of time rather than simultaneously.

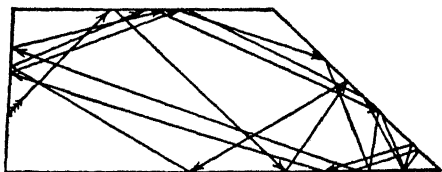


FIG. 4.

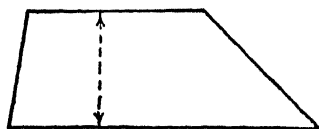


FIG. 5.

It is obvious that a single molecule reflected from the walls of a containing vessel travels equally often in any direction, as was originally stated (Fig. 4). Exception to this must be made in the case of certain special periodic motions (Fig. 5) which, however, revert to the usual behaviour upon the slightest disturbance.

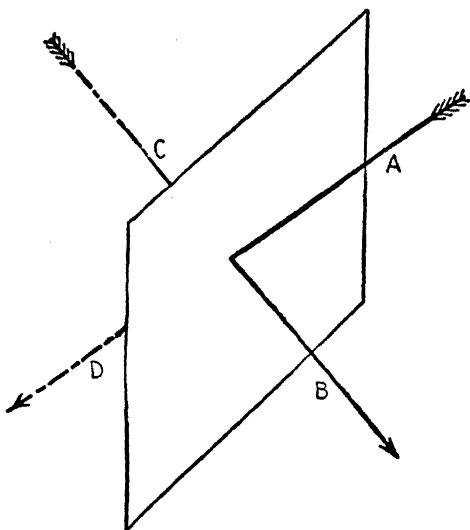


FIG. 6.

After these general remarks, it will now be shown that the isotropic distribution of velocities is not affected by the shape of the containing vessel. To do this it will first be demonstrated that if such a distribution is present it will remain unchanged upon the introduction of a plane surface into the gas (Fig. 6).

Consider a molecule,  $a$ , approaching from the right along the path  $A$ . According to the law of reflection this molecule bounces off the plane along the path  $B$ . Now there is always another molecule,  $b$ ,<sup>2</sup> which ap-

proaches the plane from the left along the path  $C$ , where  $C$  has the same direction as  $B$ .

<sup>2</sup> As a result of the isotropic distribution there are just as many molecules of type  $b$  as there are of type  $a$ . Naturally, the directions are not *exactly* fixed.

The molecule  $b$  bounces off along the path  $D$  which is  $A$  produced. In the absence of the surface the molecule  $a$  would traverse the path  $A + D$  and the molecule  $b$  the path  $C + B$ . On account of the presence of the surface,  $a$  moves along  $A + B$  and  $b$  along  $C + D$ . Thus, the only effect of the presence of the surface is to exchange the identities of the molecules in a definite path, i.e. moving in a definite direction. The molecule,  $a$ , accordingly, moves on  $B$  instead of the molecule  $b$ , and the sequence of events is changed. Neither of these circumstances is of importance. Therefore, the introduction of a plane surface does not disturb an existing uniform distribution of directions of motion. A non-uniform distribution, such as is present in a *flowing* gas, is obviously changed, since the deflected molecules are not compensated by those on the other side. A solid surface, accordingly, influences the flow of gases.

Furthermore, the conclusion is still valid if the plane is replaced by any irregular solid body, but in this case groups of more than two molecules must be considered. It must be noted that it has been unnecessary to refer to the collisions between molecules in the foregoing demonstration.<sup>3</sup>

It has just been shown that the insertion of a plane surface into a gas originally possessing a uniform distribution of directions of velocities, causes no change in this distribution. The same statement holds true for the wall of the containing vessel. If a uniform distribution obtains at any wall, the presence of the wall does not alter the distribution, but acts as if the mirror image of the actual gas were on the other side. In the case of gas flow, however, the effect of the wall cannot be neglected.

**(3) The Number of Collisions with the Wall. A More Exact Calculation of the Pressure:** The calculation of the pressure of the gas may now be made more exact by a consideration of those molecules which approach the wall of the container at an angle. Consider a system of space polar coordinates, the origin placed on the wall and the polar axis perpendicular to it (Fig. 7).

The number of molecules colliding with 1 sq. cm. of the wall in unit time and coming from the direction  $\vartheta, \varphi$  will now be calculated. Here, of course, by the direction  $\vartheta, \varphi$  is meant the cone of solid angle  $d\omega = \sin \vartheta d\vartheta d\varphi$  circumscribed about the direction  $\vartheta, \varphi$ . Obviously, only those molecules which possess velocities in this direction can come from this direction. The number of molecules in 1 cm<sup>3</sup> will be designated by  $N/v$ , where  $N$  is the total number of molecules and  $v$  is the total volume. Of these  $\frac{N d\omega}{v 4\pi}$  have the given direction.

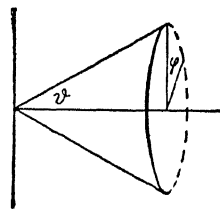


FIG. 7.

<sup>3</sup> This demonstration disproves the contentions of A. Fairbourn (*Phil. Mag.*, **43**, 1047 [1922]; also H. H. Platt, *ibid.*, **45**, 415 [1923]). Fairbourn attempted to show that differences of pressure would be set up by the introduction of a funnel-shaped solid into an attenuated gas. He neglected, however, the compensating effect of collisions on the outside of the funnel. See also R. d'E. Atkinson, *Nature*, **111**, 326 (1923); E. Witmer, *Phil. Mag.*, **47**, 152 (1924); J. Fisher, *ibid.*, **47**, 779 (1924).



Those molecules whose velocities possess the prescribed direction and which are contained in an inclined cylinder, erected on an area of  $1 \text{ cm}^2$ , of length  $w$ , and

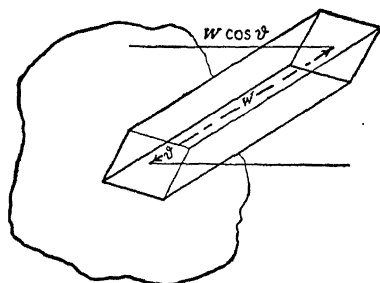


FIG. 8.

axis along the given direction (Fig. 8) will collide with the wall in one second. This is apparent since the last molecule, which was originally at the end of the cylinder, has, after one second has elapsed, traversed a length of  $w \text{ cm.}$  and hence has just collided. Those in front of it clearly reached the wall earlier. Since collisions between molecules merely exchange individuals and do not affect the number of molecules in this group, such collisions need not be taken into account. The volume of the cylinder

is  $w \times 1 \text{ cm}^2 \times \cos \vartheta$ ; therefore the number of molecules coming from the given direction is

$$\frac{N}{v} w \cos \vartheta \frac{d\omega}{4\pi} = \frac{N}{4\pi v} w \cos \vartheta \sin \vartheta d\vartheta d\varphi \quad (3.1)$$

The total number of collisions per unit area of the wall in unit time is found by integration over the hemisphere, giving  $\varphi$  the limits  $0$  to  $2\pi$  and  $\vartheta$  the limits  $0$  to  $\pi/2$ , the result being  $wN/4v$ .

In the calculation of the pressure it is to be observed that on collision with the wall only the normal component,  $w \cos \vartheta$ , of the velocity is reversed, the tangential component remaining unchanged. The change of momentum per collision is therefore  $2mw \cos \vartheta$ .

For all the collisions by molecules coming from the direction  $\vartheta$ ,  $\varphi$ , per second, it is

$$\frac{N}{v} 2mw \cos \vartheta \frac{w}{4\pi} \cos \vartheta \sin \vartheta d\vartheta d\varphi \quad (3.2)$$

which after integrating becomes  $Nmw^2/3v$  as in the approximate calculation (Equations [1.5] and [1.6]). This accidental agreement is caused by the appearance of  $\cos^2 \vartheta$  in the expression for the pressure, the average value of this term over the hemisphere being

$$\overline{\cos^2 \vartheta} = \frac{\int_0^{\pi/2} \cos^2 \vartheta \sin \vartheta d\vartheta \int_0^{2\pi} d\varphi}{2\pi} = \frac{1}{3} \quad (3.3)$$

The exact calculation of the number of collisions contains

$$\frac{1}{2} \overline{\cos \vartheta} = \frac{1}{4} \quad (3.4)$$

whereas the approximate calculation would have given  $1/6$ .

(4) **Equalization of Velocities. Temperature:** Collisions between the molecules have been disregarded until now, except when used to give a uniform distribution of *directions* of motion. They are also influential in determining the magnitudes of the velocities. Even if, as has been previously assumed, all the molecules of a gas had exactly the same speed, collisions would soon change this state, exactly as in Section 2 the one-dimensional motion was transformed into some other distribution. For the sake of simplicity the molecules will be assumed to be smooth, perfectly elastic spheres in the following discussion. The laws governing the collisions between such spheres are readily stated as follows: If the centers of two colliding spheres are connected at the moment of collision by the "line of centers," the components of the two velocities perpendicular to this direction remain unchanged, while the components along the line of centers after collision are connected with the components before collision by the relations

$$w_{1z} = \frac{m_1 - m_2}{m_1 + m_2} w_{1z}^i + 2 \frac{m_2}{m_1 + m_2} w_{2z}^i \quad (4.1)$$

$$w_{2z} = \frac{m_2 - m_1}{m_1 + m_2} w_{2z}^i + 2 \frac{m_1}{m_1 + m_2} w_{1z}^i \quad (4.2)$$

If the two masses are equal, the velocity components along the line of centers are merely interchanged. In this case it is easily shown how two originally equal speeds may be changed upon collision. Suppose two molecules collide in the manner shown in Fig. 9.

The entire initial speed of the first is parallel to the line of centers. The second has an equal speed perpendicular to that of the first, thus having no component of velocity parallel to the line of centers. After the collision the first sphere has no velocity parallel to the line of centers. The component perpendicular to this remains unchanged; since this latter component was originally zero, the sphere is brought to a complete stop. The velocity of the second is the sum of two equal and perpendicular components. The molecule is therefore deflected from its original path through  $45^\circ$  and moves off with a speed  $\sqrt{2}$  times as great as its original speed. The collisions accordingly change the velocities of the molecules not only in direction but also in magnitude.

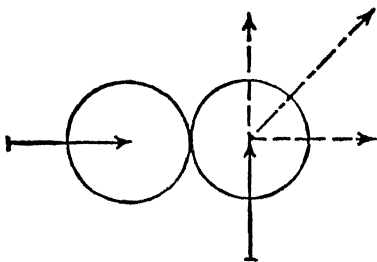


FIG. 9.

A slightly different treatment of the collision between two molecules of masses  $m_1$  and  $m_2$  will be useful later. Let the components of the velocity of the two kinds of molecules before collision, be  $\xi_1, \eta_1, \zeta_1$  and  $\xi_2, \eta_2, \zeta_2$ . It is then useful to introduce the velocity of the center of gravity, viz.,

$$\xi_c = (m_1 \xi_1 + m_2 \xi_2) / (m_1 + m_2) \quad (4.3)$$

and two other components, and also the components of the relative velocity of the two molecules with respect to each other, viz.,

$$\bar{w}_x = \xi_1 - \xi_2 \quad \bar{w}_y = \eta_1 - \eta_2 \quad \bar{w}_z = \zeta_1 - \zeta_2 \quad (4.4)$$

Direct calculation shows that

$$\begin{aligned} \frac{1}{2}m_1(\xi_1^2 + \eta_1^2 + \zeta_1^2) + \frac{1}{2}m_2(\xi_2^2 + \eta_2^2 + \zeta_2^2) \\ = \frac{1}{2}(m_1 + m_2)(\xi_c^2 + \eta_c^2 + \zeta_c^2) + \frac{1}{2}m_1m_2/(m_1 + m_2)\bar{w}^2 \end{aligned} \quad (4.5)$$

This means that the total kinetic energy of the two molecules can also be represented as two kinetic energies: one, that of a point of mass  $(m_1 + m_2)$  moving with the speed of the center of gravity, the other, that of a point of mass  $m_1m_2/(m_1 + m_2)$ , i.e., the effective mass, moving with the relative velocity  $\bar{w}$ . Since in a collision (elastic collision) the total kinetic energy and the motion of the center of gravity are not affected, it follows that  $\bar{w}$  is also unchanged, and the only effect of the collision is to change the direction of the relative velocity.

In any case, however, the kinetic energy of the whole gas is equal to the sum of the kinetic energies of the constituent molecules. In the pressure equation there must now be inserted

$$\frac{N}{N_A} E_k = \frac{\sum m w^2}{2} \quad (4.6)$$

instead of

$$\frac{N}{N_A} E_k = \frac{N m \bar{w}^2}{2} \quad (4.7)$$

where the summation is to be extended over all the molecules. Moreover, the "mean square velocity" may be defined by

$$\overline{w^2} = \frac{\sum w^2}{N} \quad (4.8)$$

$$\frac{N}{N_A} E_k = \frac{N m \overline{w^2}}{2} \quad (4.9)$$

The relation between the kinetic energy,  $E_k$ , and the temperature will now be considered. The fundamental fact necessary for the definition of temperature is that, according to experience, when two bodies are placed in "thermal contact" the exchange of energy ceases after a sufficiently long time. When in this state the two bodies are, by definition, said to have the same temperature. On the other hand, the scale by which numbers may be given to different temperatures is a matter of pure convention.

Accordingly, the relation between the mean energies  $(m_1 \overline{w_1^2}/2$  and  $m_2 \overline{w_2^2}/2)$  of the molecules of two gases in thermal equilibrium must now be found. The total number of molecules is unimportant since a decrease in the number of molecules present, together with a corresponding decrease in volume, in no

way affects the collisions or, therefore, the energy transfer. It is possible to proceed in two ways.

In the first place it may be stated that it is known from experiment that if two gases have the same pressure-volume product and if their two masses are proportional to their respective molecular weights (in which case they contain the same number of molecules since  $Nm$  equals the total weight), then the two gases are in thermal equilibrium and are therefore, by definition, at the same temperature.<sup>1</sup> But since it has been shown that

$$\frac{3pv}{2N} = \frac{mw^2}{2} \quad (4.10)$$

it follows from the equality of  $pv/N$  for all gases at the same temperature that  $mw^2/2$  is the same for all gases at a given temperature, regardless of the individual values of pressure and volume (or density), and the nature of the gas. From this it follows that for all gases  $mw^2/2$  is a function of the temperature alone and, moreover, is the same function for all gases. That this quantity should be made proportional to the temperature, or, more precisely, that

$$\frac{mw^2}{2} = \frac{3RT}{2N_A} \quad (4.11)$$

where  $R$  is the gas constant and  $N_A$  the number of molecules contained in one mole, is a purely arbitrary choice by which the volume of the gas in a constant pressure gas thermometer is taken to be directly proportional to the absolute temperature.

This demonstration gives no kinetic explanation of the fact that no heat is exchanged between two gases if their molecules have, on the average, equal amounts of energy. It has only been stated that the theory must lead to this conclusion in order that it shall agree with experience.

The second method of arriving at a kinetic definition of temperature is to deduce kinetically the foregoing law and therewith prove the empirical relation

$$pV = RT \quad (4.12)$$

where  $V$  is the volume of one mole. Consider first two different gases which have the same molecular weight and which are confined in the same container. In the course of time their average energies will become equal. To show this, suppose that the molecules of the first gas originally possessed an average energy greater than that associated with the molecules of the second. It is apparent

<sup>1</sup> The following procedure is more exact. Two equal quantities of the same gas exchange no heat if they have the same pressure-volume product. A second gas may now be brought to such a condition that, if placed in thermal contact with the first, there will be no heat transfer. By suitable adjustment of the mass of this second gas it may be made to have the same pressure-volume product as the first. It is then found that the masses of the two gases are in the ratio of small multiples of the two combining weights. If this ratio of the masses has been determined for any given value of the pressure-volume product, it remains constant for all values of the pressure-volume product. (Avogadro's law.)

that if in any gas a molecule acquires an especially high velocity, it will soon distribute this velocity among the other molecules. The result of a collision, however, depends only on the masses of the colliding spheres and not on their size and other properties. Therefore the high velocities of the molecules of the first gas will be distributed among the molecules of the second and at equilibrium the two types of molecules will have the same average energy per molecule because the only property of the molecule which enters into the equations of collision is its mass.

It will now be supposed <sup>2</sup> that the gases are at different densities and separated by a medium which will permit conduction of heat in such a way that the mechanism of this conduction can be completely understood. For this

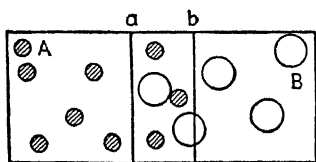


FIG. 10.

purpose the "thermal" contact between the two gases A and B (Fig. 10) will be made through a thin layer of gas separated from the gas A by the wall *a*. This wall is supposed to offer no resistance to the free passage of the molecules of gas A, but is to be completely impermeable to molecules of gas B.<sup>3</sup> Similarly the dividing wall

between the thin layer and the main body of gas B is to be permeable to gas B and is impermeable to gas A. The containing vessel for gas A reaches to the wall *b* (since *a* offers no resistance to the molecules A) and in the intermediate layer A has the same density as in its container proper. Similar statements hold for gas B with respect to wall *a*.

If it is now assumed that the molecules A have originally a higher mean velocity than those of gas B, some of the molecules of A in the intermediate space will collide with molecules of B and in this manner lose energy according to the previous discussion, because the intermediate space is simply a mixture of A and B, and it is naturally immaterial to the individual collisions whether or not containers of the pure gases are attached to the outside of the container of the mixture. As the result of the collisions in the intermediate layer the molecules of A are returned to the main body of A with less energy, on the average, than that with which they left. Those molecules which have remained in the A compartment give up energy to the returning molecules by means of collisions, that is, the returning molecules take up energy and re-enter the intermediate space with an amount of energy greater than that with which they left but which is less than their original energy. On the other hand the molecules of gas B return from the intermediate layer with an increased energy which they proceed to give up to the other molecules in the B compartment. It is seen that the intermediate layer exchanges heat from one gas to the other without disturbing the given differences in density. This heat transfer takes place from the gas of high kinetic energy to the gas of low kinetic energy.

<sup>2</sup> L. Boltzmann and G. Bryan, *Wien. Ber.*, 103, 1125 (1894); *Proc. Phys. Soc.*, 13, 485 (1895).

<sup>3</sup> Whether or not it is possible to make such a wall is beside the point. It is only necessary that the discussion does not contradict itself.

The two gases are in thermal equilibrium only if the molecules of one gas transfer no energy in the intermediate space to the molecules of the other. The exchange of heat in the intermediate layer stops, however, only when the molecules of gas *A* and gas *B* each have the same average kinetic energy.

*It has thus been proven kinetically that two gases of the same molecular weight are in thermal equilibrium (and are therefore at the same temperature) if the average kinetic energies of their molecules are equal.*

This proof must now be extended in two directions. It must first be shown that the result is independent of the nature of the heat conducting wall. This, however, would require a general knowledge of such walls. Since the theory of gases gives no information on the subject, this generalization can only be made by means of the methods of general statistical mechanics. Secondly, it must be shown that in a mixture of gases of different molecular weight each constituent has, on the average, the same mean kinetic energy per molecule. If this be proven, it can be demonstrated exactly as before that when two gases are in thermal contact they do exchange heat only if their molecules have different mean kinetic energies. In other words, it is proven that for all gases, regardless of nature and density, the temperature is determined by the kinetic energy alone. It is then natural to set the temperature proportional to the energy. However the proof of the equalization of energy in a mixture of gases of different molecular weights can only be carried out after Maxwell's law of the distribution of velocities (Sections 14, 15) has also been proven.<sup>4</sup> Until that time the general validity of the equation

$$\frac{2}{3} \cdot \frac{N_A \overline{m w^2}}{2} = RT \quad (4.13)$$

must be assumed from experience. From it the equalization of energy in mixtures of gases follows without restrictions.

Dalton's Law of Partial Pressures follows at once from this result. It has already been shown in Section 1 that, in a mixture of gases,

$$p = \frac{N_1}{v} \cdot \frac{m_1 \overline{w_1^2}}{3} + \frac{N_2}{v} \cdot \frac{m_2 \overline{w_2^2}}{3} + \dots \quad (4.14)$$

That is, the total pressure is built up of the partial pressures

$$p_1 = \frac{N_1}{v} \cdot \frac{m_1 \overline{w_1^2}}{3}, \quad p_2 = \frac{N_2}{v} \cdot \frac{m_2 \overline{w_2^2}}{3}, \quad \text{etc.} \quad (4.15)$$

Each of these partial pressures is, however, the pressure which would be exerted by the corresponding gas if it were present alone with a temperature and volume equal to the given temperature and volume because, as has just been demonstrated, the quantity  $m_i \overline{w_i^2}/2$  depends only on the temperature and not upon the density or presence of another gas.

<sup>4</sup> The proof indicated by Gans-Weber, *Repertorium der Physik* (Leipzig, 1916), I, 2, p. 366, requires the distribution law; cf., L. Boltzmann, *Wien. Ber.*, 94, 613 (1886).

(5) **The Kinetic Energy and Heat Capacity of a Monatomic Gas:** The total energy content of those molecules which may be regarded as points is the kinetic energy just discussed, which is

$$E_k = \frac{3}{2}RT \quad (5.1)$$

The molar heat capacity at constant volume is therefore

$$= \left( \frac{\partial E}{\partial T} \right)_v = \frac{3}{2}R \quad (5.2)$$

The energy content and heat capacity at constant volume are independent of the volume because the only energy associated with the gas is the mean kinetic energy of the molecules, which depends only on the temperature. Since it is known experimentally that many gases have higher heat capacities than that calculated above, it is concluded that such gases contain other types of energy. It will be shown later that these are contributed by the rotation of the molecules and motions within the molecules.

The kinetic energy of the translatory motion can be resolved along the three axes of an arbitrarily oriented system of coordinates. If this is done, then

$$w^2 = \xi^2 + \eta^2 + \zeta^2 \quad (5.3)$$

where  $\xi$ ,  $\eta$ ,  $\zeta$  are the components of  $w$  along the  $X$ ,  $Y$ , and  $Z$  axes respectively. Then

$$E_k = N_A \frac{m}{2} \overline{w^2} = \frac{m}{2} \sum w^2 = \frac{m}{2} \sum (\xi^2 + \eta^2 + \zeta^2) = \frac{N_A m}{2} (\overline{\xi^2} + \overline{\eta^2} + \overline{\zeta^2}) \quad (5.4)$$

Since, on the average, no particular direction can be especially favored,

$$\overline{\xi^2} = \overline{\eta^2} = \overline{\zeta^2} = \frac{\overline{w^2}}{3} \quad (5.5)$$

A more rigorous proof of this statement may be obtained by using the methods of Section 3. Since  $\xi = w \cos \vartheta$ ,  $\overline{\xi^2} = \overline{w^2 \cos^2 \vartheta}$ . The averaging over the directions has been carried out previously and since

$$\overline{\cos^2 \vartheta} = \frac{1}{3} \quad (5.6)$$

$$\overline{\xi^2} = \frac{1}{3} \overline{w^2} \quad (5.7)$$

The magnitude of  $w$  is still to be averaged, as indicated by the bar over the symbol  $w$ .<sup>1</sup> The particular orientation of the axes is unimportant since, on the average, the directions of the molecular velocities are distributed uniformly.

The mean kinetic energy associated with each axis is

$$\frac{3}{2} \frac{RT}{3} = \frac{RT}{2} \quad (5.8)$$

<sup>1</sup> That  $w$  is not the same for all molecules at a given instant will be shown in Section 7. Cf. also Section 4.

Thus a "one-dimensional gas" would have a heat capacity of  $R/2$ . For a two dimensional gas, whose molecules are constrained to move in a plane,

$$C_v = 2R/2$$

The mean square velocity of the molecules can now be calculated, since

$$E_k = N_A m \frac{\overline{w^2}}{2} = M \frac{\overline{w^2}}{2} = \frac{3}{2} RT \quad (5.9)$$

With  $R = 8.314 \times 10^7$  ergs/degree/mole, there is obtained

$$\overline{w^2} = 2.494 \times 10^8 \frac{T}{M} \text{ cm}^2/\text{sec}^2 \quad (5.10)$$

For hydrogen at  $0^\circ\text{C}$ ,  $\sqrt{\overline{w^2}} = 1838$  m/sec. For other gases and temperatures this quantity may be calculated from the fact that it is directly proportional to the square root of  $T$  and inversely proportional to the square root of the molecular weight.

(6) **The Work Done by the Expansion of a Gas:** The thermodynamically important process of the expansion of a gas will now be treated from the kinetic viewpoint. The two fundamental cases of adiabatic expansion to be considered are the irreversible process in which the work done equals zero and the reversible process in which a definite amount of work is performed.

For the discussion of the first case, which is realized in the Gay-Lussac experiment, consider a thermally insulated vessel divided into two parts. One half of the vessel is filled with a moderately dilute gas, the other half evacuated. Internal equilibrium is assumed to have been established in the gas. The dividing wall is now quickly removed in its own plane, in the manner of a sliding door. The molecules moving toward the empty half are in no way affected by this removal. The only change produced in the system is that they can now move further and are not reflected back again until they encounter a wall of the formerly empty half. Their kinetic energy remains unchanged but, especially in the previously evacuated portion, there is now a favored direction of velocity.<sup>1</sup> This, however, is soon obliterated by the collisions between the molecules. The increase in volume has in no way affected the magnitude of the molecular velocities, and therefore the kinetic energy of the gas is unchanged. Since the temperature of the gas is determined by the kinetic energy alone, the experiment causes no permanent temperature change. On the other hand, this conclusion could have been assumed and the fact that the kinetic energy of a gas depends only on the temperature, that is, is independent of the density, could have been derived from the experimental result.

<sup>1</sup> The excess of molecules with a velocity along the favored direction must arise at the expense of the number of molecules with velocities along the other directions. During the motion, therefore, the kinetic energy of the chaotic motion, and hence the temperature, is decreased, as a result of the mass motion of the gas.



If work is done during the expansion of the gas the situation is quite different. Consider, as in Section 1, a single molecule moving exactly perpendicular to the piston shown in Fig. 1.<sup>2</sup> The piston is moved out with the velocity  $w'$ . In the treatment of collisions with the piston it is necessary to use the velocity of the molecule relative to the piston. The molecule which has an absolute velocity  $w$  (absolute, that is, with respect to the containing vessel) has a velocity relative to the piston equal to  $w - w'$ . Upon collision with the piston it is not brought to absolute rest, but only to rest with respect to the piston, i.e. it continues to move for a short time in contact with the piston. The momentum given to the piston is therefore

$$m(w - w') \quad (6.1)$$

The same amount of momentum is again given to the piston upon the recoil of the molecule. The total momentum gained by the piston is therefore

$$2m(w - w') \quad (6.2)$$

The molecule rebounds with a velocity relative to the piston equal to  $w - w'$ . Its absolute velocity has been decreased to  $w - 2w'$ .<sup>3</sup> The kinetic energy of the molecule has been decreased by an amount equal to <sup>4</sup>

$$\frac{mw^2}{2} - \frac{m(w - 2w')^2}{2} = 2mw'(w - w') \quad (6.3)$$

If  $Zdt$  is the number of collisions with the piston in the time  $dt$ , the energy decrease of the gas in the same time is

$$- dE = 2mw'(w - w')Zdt \quad (6.4)$$

On the other hand it has been shown that the force on the piston is

$$2m(w - w')Z \quad (6.5)$$

The work done by the molecule upon the piston is this force times the displacement of the piston  $w'dt$  and is thus shown to be equal to the decrease in energy of the gas, (Equation [6.4]), as is demanded by the law of conservation of energy.

The rate of the energy decrease may also be ascertained. It is necessary for this that the process be carried out reversibly or quasistatically, that is,  $w'$  is negligibly small compared to  $w$ . The decrease in the energy of a molecule

<sup>2</sup> In other words, a one dimensional gas is assumed, the piston being drawn out in the direction of motion of the gas molecules.

<sup>3</sup> This may also be shown as follows. The initial momentum of the molecule in the direction of motion of the piston is  $mw$ . The momentum given to the piston equals  $2m(w - w')$ . The momentum remaining with the molecule is the difference of  $mw - 2m(w - w') = -m(w - 2w')$ . The molecule accordingly moves in the opposite direction with a velocity  $w - 2w'$ .

<sup>4</sup> R. Clausius, *Pogg. Ann.*, **100**, 366 (1857); *Mechanische Wärmetheorie* (2d ed., Brunswick, 1891), III, p. 29; A. Krönig, *Pogg. Ann.*, **99**, 322 (1856) (the latter paper is qualitative).

upon collision is then  $2mw'w$ . The number of collisions with the piston may be calculated with sufficient accuracy by putting it equal to the number of collisions with a stationary piston. This quantity is  $(w/2l_1)dt$ . The total decrease in energy in the time  $dt$  is therefore

$$-d\left(\frac{mw^2}{2}\right) = 2mw'w \frac{w}{2l_1} dt \quad (6.6)$$

In the same time the piston has been displaced an amount  $dl_1 = w'dt$ . Thus,

$$-\frac{d\frac{mw^2}{2}}{dl_1} = \frac{m\frac{w'w^2}{l_1}dt}{w'dt} = \frac{mw^2}{l_1} \quad (6.7)$$

or

$$-\frac{d\frac{mw^2}{2}}{mw^2} = \frac{dl_1}{l_1} \quad (6.8)$$

Upon integrating

$$-\ln(mw^2) = 2\ln l_1 + \text{const.} \quad (6.9)$$

or, since  $mw^2$  is in this case equal to  $pl_1l_2l_3$ , and  $l_1 = v/l_2l_3$ , upon changing the form of the integration constant, the equation for the reversible adiabatic expansion of a gas is found to be

$$pv^3 = p_0v_0^3 \quad (6.10)$$

If, instead of a single molecule, there are any number  $N$ , which do not collide with each other,  $Nm$  appears in the place of  $m$  throughout the demonstration and the final relation remains unchanged.

Equation (6.10) is interesting in several respects. In the first place it shows how a finite amount of work may be done even though the piston is moved infinitely slowly as required by the condition of reversibility. For although by (6.3) the work done in a single collision is directly proportional to the piston velocity,  $w'$ , and is therefore infinitely small, the number of collisions for a given displacement is inversely proportional to  $w'$  and, for an infinitely slow motion, becomes infinitely large. Thus, in Equation (6.7), which gives the work done for a given piston displacement (volume change),  $w'$  appears in both numerator and denominator and hence cancels out. The equation of the reversible adiabatic change developed in thermodynamics is

$$pv^{C_p/C_v} = p_0v_0^{C_p/C_v} \quad (6.11)$$

In the present instance, therefore,  $C_p/C_v$  must equal 3. This is in fact the case, since the considerations have dealt with a one dimensional gas for which

$$C_v = \frac{1}{2}R \quad \text{and} \quad C_p = C_v + R = \frac{3}{2}R$$

Equation (6.10) is therefore in complete agreement with thermodynamics.

In the case of a three dimensional gas only the component of velocity normal to the piston is diminished; the components in the plane of the piston remaining unchanged during a collision. The decrease in energy per collision then becomes  $2mw' \cos \vartheta$ . The collisions between the molecules, if the piston velocity is sufficiently low, preserve the uniform distribution of the velocities which would otherwise be disturbed by the motion of the piston.

The decrease in energy during the displacement  $dl_1$ , is

$$-\frac{d \frac{Nmw^2}{2}}{dl_1} = \frac{Nmw^2}{l_1} \frac{1}{\cos^2 \vartheta} = \frac{Nmw^2}{3l_1} \quad (6.12)$$

From this

$$-\ln(Nmw^2) = \frac{2}{3} \ln l_1 + \text{const} \quad (6.13)$$

accordingly

$$pv^{5/3} = p_0 v_0^{5/3} \quad (6.14)$$

as must now be the case.

It is further seen from the demonstration that if the piston velocity is too great to be neglected in comparison with  $w$ , the pressure and therefore also the work done is less than in the quasistatic case. Moreover, upon compression, ( $w'$  negative), the pressure and the work done on the gas are greater than in the infinitely slow process. This is also in agreement with thermodynamics.<sup>5</sup>

**(7) The Barometric Formula and Maxwell's Law of Distribution of Velocities:** Consider a column of gas at equilibrium in a constant gravitational field. It is known from thermodynamics that the whole column must be at the same temperature. Consider now a thin horizontal layer of thickness  $dx$  and cross-section equal to  $1 \text{ cm}^2$ . The weight of this layer is  $cgMdx$ , where  $g$  is the acceleration of gravity,  $c$  the number of moles/ $\text{cm}^3$ , that is,  $N/vN_A$ , and  $M$  is the molecular weight. The pressure on the under side of the layer in question is greater than that on the upper side by the amount  $cgMdx$ , or

$$-\frac{dp}{dx} dx = cgMdx \quad (7.1)$$

$x$  being measured vertically upward. Equation (7.1) is the familiar hydrostatic formula.

Further

$$p = \frac{RT}{V} = cRT \quad (7.2)$$

<sup>5</sup> A more detailed treatment of the work done in case of high piston velocity can be found in the 2d ed. of this treatise, Vol. I, p. 92. This applies to the case in which the mean free path is large compared to the dimensions of the vessel. W. and G. Meissner, *Ann. Physik*, **36**, 303 (1939), have shown that in the opposite case (mean free path small) the hydrodynamic equations (Section 17) can be used. For a practical internal combustion engine, the deviation from equilibrium is less than 1 in  $10^7$ . By using the kinetic theory value for viscosity, the two treatments give results of the same order of magnitude, if the mean free path is comparable to the length of the piston stroke.

where  $V$  is the molar volume. Accordingly

$$-\frac{d(cT)}{dx} = \frac{Mg}{R} c \quad (7.3)$$

Since the system is in thermal equilibrium,  $T$  is constant, and

$$\ln c = -\frac{Mg}{RT}x + \ln c_0, \quad c = c_0 e^{-\frac{Mgx}{RT}} \quad (7.4)$$

or

$$p = p_0 e^{-\frac{Mgx}{RT}} \quad (7.5)$$

where  $c_0$  and  $p_0$  signify respectively the concentration and pressure at sea-level ( $x = 0$ ). This formula gives the decrease in atmospheric pressure with altitude. Actually, however, temperature differences are present in the earth's atmosphere due to convection currents, which cause deviations from the equilibrium state.

The discussion from the kinetic standpoint is as follows. Imagine the gas again to be one-dimensional in the  $x$ -direction, neglecting, therefore, the momenta along the  $y$ - and  $z$ -axes. The effect of collisions will also be neglected for the present. If all the molecules had the same velocity, the behavior of the gas would be quite different from that required by thermodynamics. The molecules starting up from sea level with a velocity  $w_0$  would lose their kinetic energy according to the equation

$$\frac{mw^2}{2} = \frac{mw_0^2}{2} - mgx \quad (7.6)$$

At the height  $x = w_0^2/2g$  they would all stop and fall back to the earth, finally regaining their original kinetic energy. The atmosphere would accordingly have a sharp upper limit and its temperature would decrease linearly with the altitude until it reached the absolute zero. The density, however, would increase with the altitude since, in the upper regions, the molecules would move more slowly and therefore require a longer time to traverse a given interval. These conclusions are changed slightly on taking into account the horizontal components of the velocity, but the existence of the sharp limit and the decrease of the temperature remain unchanged. To obtain agreement with the thermodynamic treatment it is therefore necessary to conclude that the molecules cannot all have the same velocity, as has already been shown from the law of collisions.

The distribution of velocities which will permit the temperature to remain constant throughout the column and at the same time satisfy Equation (7.4) will now be determined.<sup>1</sup>

Just as it was formerly necessary to speak of the number of molecules having directions of velocity within a definite solid angle, it will now be neces-

<sup>1</sup> L. Boltzmann, *Wien. Ber.*, 74, 503 (1876).

sary to consider the number of molecules having velocities whose magnitudes fall within certain limits. All the previous limitations placed upon the size of this limiting interval of velocities apply to the present case. The number of molecules having velocities between  $w$  and  $w + dw$  (where  $dw$  is only physically, not mathematically, infinitely small, cf. Section 2) will be designated by

$$dN = Nf(w)dw \quad (7.7)$$

where  $N$  is the number of molecules per cc. and  $f(w) dw$  the fraction of the molecules fulfilling the specified requirements. In this section the subscript zero attached to a symbol will indicate that the quantity is measured at the bottom of the column, the subscript  $x$  referring to a height  $x$  above the bottom. It has already been shown that if  $N'$  molecules per cubic centimeter are moving parallel to each other with the velocity  $w$ , then, in the time  $dt$ , there will pass through unit area of a plane perpendicular to the direction of motion, the number  $N'w dt$ . In other words, the molecules passing the plane in a given time are the contents of a cylinder of unit cross-section and height  $w dt$ , since the last molecule in this cylinder will just pass the plane at the end of the time  $dt$ .

Consider now two planes at the heights  $x$  and  $x + dx$ . In the upper plane the density of the molecules must, according to Equations (7.2) and (7.4), be smaller than that in the lower plane by the amount

$$N \frac{mg}{kT} dx = N_0 e^{-\frac{mgx}{kT}} \frac{mg}{kT} dx * \quad (7.8)$$

This is only possible if certain molecules can pass the lower plane but cannot reach the upper one, stopping and falling back in the intermediate space. The number of molecules thus reversed per second per unit cross-section of the layer is

$$N_x \bar{w} - N_{x+dx} \bar{w} = N_0 e^{-\frac{mgx}{kT}} \bar{w} \frac{mg}{kT} dx \quad (7.9)$$

Since the gas is at constant temperature, the mean velocity  $\bar{w}$  of the molecules is the same at all heights.

The velocities with which those molecules which are turned back bounce up from the bottom of the column must lie within such limits that the slowest can just pass the lower plane, that is

$$2 = mgx \quad (7.10)$$

while the fastest must just reach the upper plane or

$$\frac{m(w_0 + dw_0)^2}{2} - mg(x + dx) \quad (7.11)$$

\*  $k = R/N_A = mR/M$ ;  $k$  is known as the Boltzmann constant.

whence

$$w_0 dw_0 = g dx \quad \text{and} \quad w_0 = \sqrt{2gx} \quad (7.12)$$

The number of molecules per cubic centimeters having this velocity at the bottom is

$$N_0 f_0(w_0) dw_0 \quad (7.13)$$

The number leaving the bottom per second per unit cross section is

$$N_0 f(w_0) w_0 dw_0 = N_0 f_0(\sqrt{2gx}) g dx \quad (7.14)$$

after substitution of the values obtained in (7.10) and (7.12).

All these and only these molecules have as an upper limit to their paths the layer between  $x$  and  $x + dx$ . Upon reaching this layer, they fall back again. Equating (7.9) and (7.14) there is obtained

$$N_0 \bar{w} \frac{mg}{kT} e^{-\frac{mgx}{kT}} dx = N_0 f_0(\sqrt{2gx}) g dx \quad (7.15)$$

or

$$f_0(\sqrt{2gx}) = \frac{\bar{mw}}{kT} e^{-\frac{mgx}{kT}} = \frac{\bar{mw}}{kT} e^{-\frac{m}{2kT} (\sqrt{2gx})^2} \quad (7.16)$$

or

$$f_0(w_0) = \frac{\bar{mw}}{kT} e^{-\frac{mw_0^2}{2kT}} = A e^{-\frac{mw_0^2}{2kT}} \quad (7.17)$$

This is the simplest form of the famous Maxwell distribution law<sup>2</sup> which plays an outstanding part in the whole of the kinetic theory. The preceding discussion has only proved, however, that this relation must hold in order that the thermodynamic requirement of constancy of temperature be satisfied for a column of gas in equilibrium in a gravitational field, but no proof of this distribution law has been given on kinetic grounds. This proof, when given (Sections 14, 15), will be a kinetic explanation of the thermodynamical statement.

This distribution of velocities is clearly not the result of the gravitational field, since the strength of the field,  $g$ , does not appear in the formula. The effect of gravity is merely to separate the molecules into a "velocity spectrum."

Since the temperature is constant, the same distribution of velocities exists throughout the entire column, that is, the relation

$$dN = N A e^{-\frac{mv^2}{2kT}} dv \quad (7.18)$$

represents the relative distribution of the velocities among the molecules. The quantity  $dN/N$  everywhere remains the same for a given value of  $w$ , only the *absolute* number of molecules varying with the height. Since, however, it may seem paradoxical that the *mean* kinetic energy is the same for different altitudes, the cause of this fact will be further explained.

<sup>2</sup> Clerk Maxwell, *Phil. Mag.*, 19, 22 (1860).

Roughly speaking the total kinetic energy of a group of molecules is decreased as the group moves upward, but at the same time the number of molecules is decreasing due to the dropping out of the slower ones. This dropping out takes place in such a manner that the average kinetic energy per molecule remains constant.<sup>3</sup> This constancy is made possible by the particular form of Maxwell's law, from which it follows that if  $dN$  is plotted<sup>4</sup> as a function of  $w^2$  and part of the curve cut off by erecting a new ordinate axis at  $w_1^2$ , the curve to the right of the new axis is equivalent to that which would be obtained if the energy of each molecule were decreased by a constant amount. It is now seen that the right hand portion of the curve again represents a Maxwellian distribution of the remaining molecules (Fig. 11). Geometrically this means that the curve lying to the right of the new axis is a replica, on a smaller vertical scale, of the original curve.

Throughout this discussion it has been assumed that the molecules move only in a vertical direction and that they do not collide with each other. These limitations will now be removed successively. If, in the first place, the

<sup>3</sup> Perhaps this may be further clarified by the following example: Coins (energy) are distributed among a number of people (molecules) according to an exponential law. Then

Number of coins ( $E$ ) per person.....	0	1	2	3	4	5	6
Number of persons possessing $E$ coins.....	64	32	16	8	4	2	1

The equation expressing this distribution is

$$64 \times 2^{-E} = 64e^{-E \ln 2}$$

The average number of coins possessed per person is

$$\frac{64 \times 0 + 32 \times 1 + 16 \times 2 + 8 \times 3 + 4 \times 4 + 2 \times 5 + 1 \times 6}{64 + 32 + 16 + 8 + 4 + 2 + 1} = \frac{120}{127} = 0.945$$

If one coin is taken from each person except the 64 who already have none, the distribution is

Number of coins ( $E$ ) per person.....	0	1	2	3	4	5
Number of persons possessing $E$ coins.....	32	16	8	4	2	1

and the equation of this distribution is

$$32 \times 2^{-E} = 32 \times e^{-E \ln 2} = 64 \times e^{-1 \ln 2} e^{-E \ln 2}$$

Barometric      Energy  
formula      distribution

The average number of coins per person is now

$$\frac{32 \times 0 + 16 \times 1 + 8 \times 2 + 4 \times 3 + 2 \times 4 + 1 \times 5}{32 + 16 + 8 + 4 + 2 + 1} = \frac{57}{63} = 0.905$$

The two figures for the average number of coins possessed per person (mean energy) do not agree exactly because the series is stopped after seven terms. If the next term be taken into account by giving half a person 7 coins in the first case and 6 in the second ("half a person" means one having 7 coins half the time and none for the remainder of the time, cf. Section (2)), then the average possession of coins becomes in the first case  $247/255 = 0.969$  and in the second  $120/127 = 0.945$ . The disagreement is thus decreased from 4.5 to 2 per cent. The essential point is therefore that the persons (molecules) already having no coins (zero energy) drop out entirely.

<sup>4</sup>  $dN/NAdw$  is plotted as ordinate against  $0.43 mw^2/2kT$  as abscissa.

molecules moving up are allowed to collide with those coming down, the sole effect is to exchange the velocities of the colliding molecules. For example, if there are no collisions, molecule *A* moves upward with a velocity  $w_A$  and molecule *B* moves downward with velocity  $w_B$ . If, however, these two collide, molecule *A* moves downward after the collision with velocity  $w_B$  and molecule *B* moves upward with velocity  $w_A$ . Since it does not matter which individual molecule (*A* or *B*) has a certain velocity and place, the collision has produced no change in the distribution.

Finally, if horizontal velocity components are admitted, the vertical motion remains entirely unaffected. The magnitude and distribution of these horizontal components

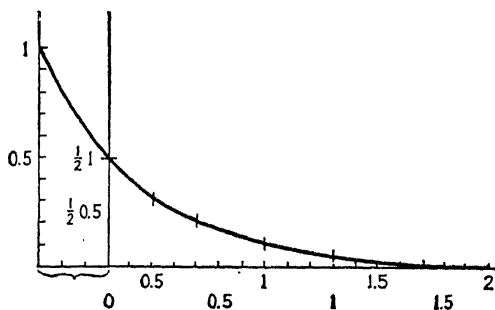


FIG. 11.

are readily deduced as follows: It has been pointed out that the distribution of velocities is independent of the strength of the gravitational field, and that the field merely brings the distribution to our attention. The distribution would remain unchanged, therefore, if there were no field in the vertical direction, but instead a constant field in the  $y$ -direction. Then, just as before, in order that the temperature remain constant along the  $y$ -axis at equilibrium, the velocity component  $\eta$  must be distributed according to the Maxwell law

$$dN = N_0 A e^{-\frac{m\eta^2}{2kT}} d\eta \quad (7.19)$$

A similar argument holds for  $\zeta$ , the component in the  $z$ -direction.

(8) **A More Exact Discussion of Maxwell's Law:** Let us return again to the one-dimensional gas. The number of molecules having velocities between  $\xi$  and  $\xi + d\xi$  is

$$dN = A e^{-\frac{m\xi^2}{2kT}} d\xi \quad (8.1)$$

The numerator and denominator of the exponent may each be multiplied by  $N_A$  giving

$$\frac{N_A m \xi^2}{2N_A k T} = \frac{M \xi^2}{2RT} \quad (8.2)$$

This expression contains only quantities referring to one mole, therefore the distribution law cannot be used to calculate  $N_A$ . The constant  $A$  is evaluated from the fact that the total number of molecules present is  $N_0$ . That is

$$\int_{-\infty}^{+\infty} e^{-\frac{m\xi^2}{2kT}} d\xi = N_0 \quad (8.3)$$



The evaluation of this and similar integrals is best obtained by the change of variables

$$\frac{m\xi^2}{2kT} = x \quad \text{or} \quad \xi \sqrt{\frac{m}{2kT}} = x \quad (8.4)$$

This shows at once the manner in which  $m$  and  $T$ , the important quantities, enter  $A$ , leaving only a numerical factor to be calculated, viz.,

$$\sqrt{\frac{2kT}{m}} \int_{-\infty}^{+\infty} e^{-x^2} dx = N_0 \quad (8.5)$$

$$A = N_0 \quad 2\pi kT \quad (8.6)$$

If the distribution be represented graphically by plotting  $\xi$  as abscissa against the ordinate  $\frac{1}{N_0} \frac{dN}{d\xi}$ , a magnitude which gives the relative frequency of the different velocities, there is obtained a curve which, at  $\xi = 0$ , meets the ordinate at  $\sqrt{m/2\pi kT}$  with a horizontal tangent (Fig. 12, I). This horizontal tangent

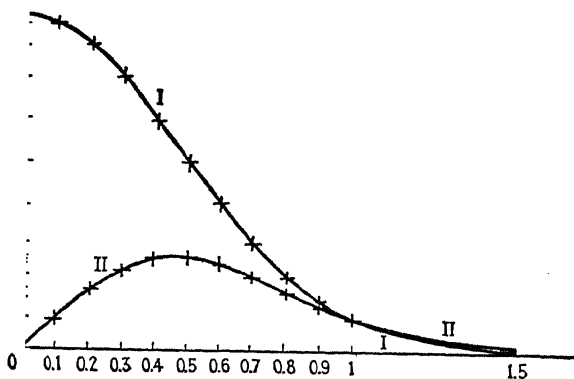


FIG. 12.

is caused by the presence of the square of  $\xi$  in the numerator of the exponent and would not appear if the energy,  $m\xi^2/2$ , were plotted as the abscissa. Fig. 12, II will be explained on p. 31.

As  $\xi$  is increased (curve I) the ordinate decreases slowly at first and then much more rapidly.<sup>1</sup> The fraction of the molecules having velocities between  $\xi$  and  $\xi + d\xi$  does not change greatly as long as  $m\xi^2/2$  is of the order of magnitude of  $kT$ . On the other hand, if  $m\xi^2/2 = 10kT$ , the ordinate is only  $e^{-10} = 10^{-4.3} \dots = \frac{1}{2} \times 10^{-4}$  times its original value; if  $m\xi^2/2 = 20kT$ ,  $\frac{1}{4} \times 10^{-8}$ , etc. The fraction of the molecules possessing an energy greater than some

<sup>1</sup> It must be borne in mind that the discussion still deals with a one-dimensional gas.

given value  $m\xi_0^2/2$  is

$$\frac{N}{N_0} \frac{\int_{\xi_0}^{\infty} e^{-\frac{m\xi^2}{2kT}} d\xi}{\int_0^{\infty} e^{-\frac{m\xi^2}{2kT}} d\xi} = 2 \sqrt{\frac{1}{\pi}} \int_{\sqrt{m\xi_0^2/2kT}}^{\infty} e^{-x^2} dx = 1 - \Phi(x_0) \quad (8.7)$$

The last integral ( $\Phi$  = Gauss error function) can only be evaluated as an infinite series. Its values have, however, been tabulated and may be found in B. O. Pierce, *A Short Table of Integrals*, Ginn and Co. (1910). Some values of the integral, for small values of the lower limit, i.e.,  $\sqrt{\text{energy}/kT}$ , are given in Table I.

TABLE I  
VALUE OF THE INTEGRAL

Lower limit, $x_0$	Integral $[1 - \Phi(x_0)]$
0 .....	1
0.1 .....	0.89
0.2 .....	0.78
0.3 .....	0.67
0.4 .....	0.57
0.5 .....	0.48
0.6 .....	0.40
0.8 .....	0.26
1 .....	0.16
1.5 .....	0.034
2 .....	$47 \times 10^{-4}$
3 .....	$22 \times 10^{-6}$
4 .....	$15 \times 10^{-9}$

The series from which the values are obtained are:

$$\left. \begin{aligned} x < 1: & \quad \frac{2}{\sqrt{\pi}} \int_0^x e^{-x^2} dx = \frac{2}{\sqrt{\pi}} \left( x - \frac{x^3}{3} + \frac{1}{2!} \frac{x^5}{5} - \frac{1}{3!} \frac{x^7}{7} + \dots \right) \\ x > 1: & \quad \frac{2}{\sqrt{\pi}} \int_0^x e^{-x^2} dx = 1 - \frac{2e^{-x^2}}{\sqrt{\pi}} \left( \frac{1}{2x} - \frac{1}{4x^3} + \frac{3}{8} \frac{1}{x^5} - \frac{15}{16} \frac{1}{x^7} + \dots \right) \end{aligned} \right\} \quad (8.8)$$

On account of the high rate of relative decrease of the curve at high values of  $\xi$ , the number of molecules having a velocity greater than a definite limit  $\xi_0$  is practically the same as the number having velocities between  $\xi_0$  and  $\xi_1 > \xi_0$ , provided that  $\xi_0$  is sufficiently large and the interval  $\xi_0$  to  $\xi_1$  is not too small. This is due to the fact that the number of molecules having velocities greater than  $\xi_1$  is relatively small.

The influence of a change of temperature upon the shape of the curve is deduced as follows. If, instead of the temperature  $T_1$ , the gas is maintained at some higher temperature  $T_2$ , the velocity  $\xi_2$  at which the exponent and therefore

the exponential term have the value previously determined by  $\xi_1$  and  $T_1$  is given by

$$\frac{m\xi_1^2}{2kT_1} = \frac{m\xi_2^2}{2kT_2} \quad (8.9)$$

Therefore  $\xi_2 > \xi_1$ , and the whole curve is extended in a horizontal direction by an amount proportional to the square root of the temperature. Since, however, the area included between the curve, the abscissa and the ordinate must always be equal to unity,

$$\frac{1}{N_0} \int \frac{dN}{d\xi} d\xi = \quad (8.10)$$

the ordinate  $A$  at  $\xi = 0$  must be diminished by the factor  $1/\sqrt{T}$  according to equation (8.6). The effect is therefore to lessen the inequality of distribution of the velocities, the number of molecules with relatively large velocities being increased to the greater extent. The total number of molecules having an energy greater than some given value, for example,  $10kT_1$  is the fraction  $7.9 \times 10^{-6}$  of all the molecules present. If the temperature is doubled, the energy value that has been assumed becomes  $5kT_2$  and  $1.5 \times 10^{-3}$  of the molecules present now have an energy equal to or greater than this value.

On the other hand, the number of molecules having a relatively small energy is much less affected by changes in temperature. Thus, those molecules having an energy greater than  $2kT$  form about 5 per cent of the total. For the same energy doubling the temperature increases this fraction to about 16 per cent.<sup>2</sup>

The mean kinetic energy is

$$\frac{\int \frac{m}{2} \xi^2 dN}{N_0} = \frac{\int_{-\infty}^{+\infty} \frac{m}{2} \xi^2 e^{-\frac{m\xi^2}{2kT}} d\xi}{\int_{-\infty}^{+\infty} e^{-\frac{m\xi^2}{2kT}} d\xi} = kT \frac{\int_{-\infty}^{+\infty} x^2 e^{-x^2} dx}{\int_{-\infty}^{+\infty} e^{-x^2} dx} = \frac{1}{2} kT \quad (8.11)$$

<sup>2</sup> The distribution of a gas in a gravitational field is entirely analogous. Here, too, there is an exponential distribution of density upwards. At a sufficiently great height it becomes immaterial whether the calculations deal with the total quantity of gas above this height or the amount of gas in a sufficiently thick finite layer, since the quantity neglected by limiting the calculation to a layer is relatively very small. The corresponding air pressure is a measure of this neglected quantity and the previous statement amounts to saying that it is not very inaccurate to use the difference in pressure between the given high altitude and a still higher one, rather than the total atmospheric pressure at a given height.

The analogy may also be extended to the effect of temperature changes. Increase in temperature decreases the differences in density, because the decrease in the exponent of Equation (7.4) lessens the influence of the exponential term or, speaking physically, because for a given density the pressure increases (Equation [7.2]) and therefore a smaller *relative* change of pressure suffices to support an equal weight.

As in the Maxwell law, the density at zero height must decrease on account of the increase of density in the upper levels, provided that the quantity of gas is constant. Formally,

The number of molecules which collide with 1 cm<sup>2</sup> of the wall in 1 sec is, according to Equation (3.1),

$$\int \xi dN = \frac{N_0 \int_0^{\infty} \xi e^{-\frac{m\xi^2}{2kT}} d\xi}{v \int_{-\infty}^{+\infty} e^{-\frac{m\xi^2}{2kT}} d\xi} = \frac{N_0}{v} \sqrt{\frac{2kT}{m}} \int_0^{\infty} x e^{-x^2} dx = \frac{N_0}{2v} \sqrt{\frac{2kT}{\pi m}} \quad (8.12)$$

If this is set equal to  $\bar{w}N_0/4v$  (see p. 10), there is obtained

$$|\bar{w}| = \sqrt{\frac{2kT}{m}} = \sqrt{\frac{2RT}{\pi M}} \quad (8.13)$$

It should be noted that the average velocity  $|\bar{w}|$  is connected with the square root of the average of the square of the velocity (root mean-square velocity  $\sqrt{\bar{w}^2}$ , Equations (4.8) and (5.10)) for a three-dimensional gas by the relation

$$|\bar{w}| = 2 \sqrt{\frac{2}{3\pi}} \sqrt{\bar{w}^2} = 0.922 \sqrt{\bar{w}^2} \quad (8.14)$$

The difference between these two quantities is due to the fact that they were obtained by different methods of averaging.<sup>3</sup> Although both are proportional to  $\sqrt{RT/M}$ , the proportionality constant differs according to the method used. This variety of proportionality constants, which occurs frequently in the deductions of the kinetic theory, will be discussed in detail below.

Upon proceeding to the case of a two dimensional gas it is to be remembered that, according to the conclusion reached in Section (7), the distribution of velocities along the  $x$ -axis is completely independent of the distribution along the  $y$ -axis. It will be shown that this is equivalent to assuming (8.1) for the  $x$  direction and, at the same time, isotropic distribution in direction.

The number of molecules simultaneously satisfying the two conditions to the effect that the  $x$ -components of their velocities lie between  $\xi$  and  $\xi + d\xi$  and their  $y$ -components between  $\eta$  and  $\eta + d\eta$ ,<sup>4</sup> may be expressed by

$$\frac{d_{\xi\eta}N}{N_0} = f(\xi, \eta) d\xi d\eta \quad (8.15)$$

The uniform distribution of directions of velocities requires that the function  $f$  depends not on the individual values of  $\xi$  and  $\eta$ , but only on the magnitude

however, a gas in a gravitational field is analogous to a two, rather than a one, dimensional gas since the distribution is  $e^{-\frac{mgx}{kT}} dx$  corresponding to Equation (8.22) and not (8.1).

<sup>3</sup> Consider two molecules, one of the velocity 1, the other of the velocity 5, their average velocity is  $|\bar{w}| = (1 + 5)/2 = 3$ . The average of the square velocity is  $\bar{w}^2 = (1 + 25)/2 = 26/2$ ,  $\sqrt{\bar{w}^2} = 3.6$ .

<sup>4</sup> The variables of differentiation are written as subscripts after the sign of differentiation. More properly,  $d^2N$  should be used.

of the total velocity. According to the parallelogram law the latter is  $\sqrt{\xi^2 + \eta^2}$ . The function, therefore, has the form  $f(\sqrt{\xi^2 + \eta^2})$ . In order to evaluate this function it will be integrated over all possible values of  $\eta$ , with  $\xi$  being held constant. The expression resulting from this integration is simply the distribution law of the  $\xi$  components alone, Equation (8.1). That is

$$\int_{-\infty}^{+\infty} f(\sqrt{\xi^2 + \eta^2}) d\eta = A e^{-\frac{m\xi^2}{2kT}} \quad (8.16)$$

Upon solving this integral equation it is found that

$$f = \frac{m}{2\pi kT} e^{-\frac{m(\xi^2 + \eta^2)}{2kT}} = \sqrt{\frac{m}{2\pi kT}} e^{-\frac{m\xi^2}{2kT}} \sqrt{\frac{m}{2\pi kT}} e^{-\frac{m\eta^2}{2kT}} \quad (8.17)$$

which states that the fraction of the molecules having simultaneously  $x$ -components of velocity between  $\xi$  and  $\xi + d\xi$  and  $y$ -components between  $\eta$  and  $\eta + d\eta$  is obtained by multiplying the fraction of all the molecules present fulfilling the first condition by the fraction fulfilling the second. The validity of such a proposition means that the components along the  $x$ -axis are completely independent of the components along the  $y$ -axis. That is, a molecule with any definite  $x$ -component  $\xi$ , has no particular preference for any (especially large or especially small)  $y$ -component  $\eta$ . The same value for the fraction of molecules with  $x$ -component between  $\xi$  and  $\xi + d\xi$  is obtained whether it is calculated for all the molecules or only those having  $y$ -components between  $\eta$  and  $\eta + d\eta$ .

The first number is given by

$$\frac{d_\xi N}{N_0} = \sqrt{\frac{m}{2\pi kT}} e^{-\frac{m\xi^2}{2kT}} d\xi \int_{-\infty}^{+\infty} \sqrt{\frac{m}{2\pi kT}} e^{-\frac{m\eta^2}{2kT}} d\eta = \sqrt{\frac{m}{2\pi kT}} e^{-\frac{m\xi^2}{2kT}} d\xi \quad (8.18)$$

and the second by

$$\left. \begin{aligned} \frac{d_{\xi\eta} N}{d_\eta N} &= \frac{\sqrt{\frac{m}{2\pi kT}} e^{-\frac{m\xi^2}{2kT}} \sqrt{\frac{m}{2\pi kT}} e^{-\frac{m\eta^2}{2kT}} d\xi d\eta}{\sqrt{\frac{m}{2\pi kT}} e^{-\frac{m\eta^2}{2kT}} d\eta} \\ &= \sqrt{\frac{m}{2\pi kT}} e^{-\frac{m\xi^2}{2kT}} d\xi \end{aligned} \right\} \quad (8.19)$$

The situation may be represented in a “ $\xi$ - $\eta$  plane,” which is a plane described by the rectangular coordinates  $\xi$  and  $\eta$  (Fig. 13). Thus for each molecule there is a “state point” designated by the coordinates  $\xi$  and  $\eta$  which are the components of the velocity of the molecule represented. The radius vector from the origin to this state point represents the molecule’s velocity both in magnitude ( $\sqrt{\xi^2 + \eta^2}$ ) and direction. The number of state points in any elementary area  $d\xi d\eta$  is given by Equations (8.15) and (8.17), whence the density

of state points at  $\xi, \eta$  is

$$N_0 \frac{m}{2\pi kT} e^{-\frac{m}{2} \frac{\xi^2 + \eta^2}{kT}} \quad (8.20)$$

The maximum density is at the origin where  $w^2 = \xi^2 + \eta^2 = 0$ . Going out from this point, the *density* decreases according to the laws which have been previously developed for a one dimensional gas. The leveling off of the density with increasing temperature is also similar to the previous case. In agreement with the foregoing assumption, it is seen that the density in the figure depends only upon the magnitude of  $w$  and not upon its direction. It is therefore frequently convenient to express the velocity in the polar coordinates,  $w$ , the magnitude, and  $\varphi$ , the angle between the velocity and the positive  $x$ -axis. An elementary area then equals  $dw w d\varphi$  and the number of points lying in this region is

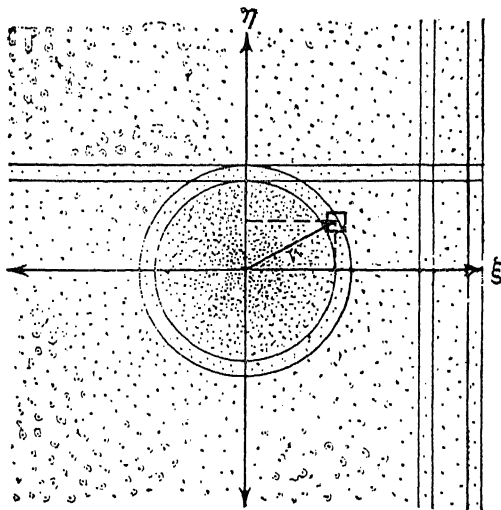


FIG. 13.

$$N_0 \frac{m}{2\pi kT} e^{-\frac{mw^2}{2kT}} w dw d\varphi$$

This is the number of molecules having velocities of magnitude between  $w$  and  $w + dw$  and a direction making an angle between  $\varphi$  and  $\varphi + d\varphi$  with the  $x$ -axis. The number of molecules with velocities of magnitudes between the given limits regardless of direction, is

$$d_w N = N_0 \frac{m}{2\pi kT} e^{-\frac{mw^2}{2kT}} w dw \int_0^{2\pi} d\varphi = N_0 \frac{m}{kT} e^{-\frac{mw^2}{2kT}} w dw \quad (8.21)$$

This is the number of molecules whose state points lie within an annulus of inner radius  $w$  and width  $dw$ , accordingly, within the area  $2\pi w dw$ . Upon plotting the magnitude  $d_w N / N_0 dw$  against  $w$  (Fig. 12, II) it is found to be zero when  $w = 0$ , and, as  $w$  increases, it rises to a maximum and then diminishes along a curve which, for large values of  $w$ , has again essentially an exponential decrease. The maximum is caused by the facts that the density continually decreases with increasing  $w$ , at first slowly and then quite rapidly, but the annular area increases linearly with  $w$ . At first, the uniform increase of the

area is relatively larger than the slow decrease of the density. At large values of  $w$  the relative importance of the two terms is reversed.<sup>5</sup> The physical meaning of this increase of area with the increase in  $w$  is that large velocities may be compounded from a great many more combinations of the two components. Thus, for example, a large velocity may be compounded from a small  $\xi$  and a large  $\eta$ , a moderate  $\xi$  and a moderate  $\eta$ , or a large  $\xi$  and a small  $\eta$ . To summarize: Figure 13 shows that a discussion of the distribution of the magnitudes of the velocities involves consideration of successive rings. It also shows that the distribution of  $x$ -components of velocity among that particular sub-group of molecules which have  $y$ -components between  $\eta$  and  $\eta + d\eta$  is given by the distribution along the horizontal strip between  $\eta$  and  $\eta + d\eta$ . It must be noted that this last *distribution* does not depend on the position  $\eta$  of the horizontal strip, just as in the case of a column of gas under the influence of gravity the relative distribution is independent of the position in the column. Finally, the distribution of the  $x$ -component alone is found by comparing the total number of points contained in the various vertical strips.

The most probable velocity, i.e., the one for which  $d_w N/dw$  has its maximum value, is given by

$$\frac{d}{dw} \left( e^{-\frac{mw^2}{2kT}} w \right) = 0; \quad \frac{1}{2}mw_{mp}^2 = \frac{1}{2}kT \quad (8.23)$$

A calculation of the average energy of the molecules of this two dimensional gas gives the result

$$\frac{1}{2}m\overline{w^2} = \frac{\int_{-\infty}^{+\infty} \frac{1}{2}mw^2 e^{-\frac{mw^2}{2kT}} w dw}{\int_{-\infty}^{+\infty} e^{-\frac{mw^2}{2kT}} w dw} = kT \frac{\int_{-\infty}^{+\infty} x^2 e^{-x^2} x dx}{\int_{-\infty}^{+\infty} e^{-x^2} x dx} = kT \quad (8.24)$$

To proceed finally to a three dimensional gas, it will merely be necessary to generalize the results which have already been obtained. Thus the number of molecules whose velocities have  $x$ -components between  $\xi$  and  $\xi + d\xi$ ,  $y$ -components between  $\eta$  and  $\eta + d\eta$ , and  $z$ -components between  $\zeta$  and  $\zeta + d\zeta$ , is given by

$$d_{\xi\eta\zeta} N = N_0 \left( \frac{m}{2\pi kT} \right)^{\frac{3}{2}} e^{-\frac{m}{2} \frac{(\xi^2 + \eta^2 + \zeta^2)}{kT}} d\xi d\eta d\zeta \quad (8.25)$$

As in the discussion of the distribution of directions of velocities it is necessary to use the "velocity space" in order to give a graphical representation. In this space each molecule has a statepoint. The radius vector from the origin

<sup>5</sup> If the distribution had been plotted against energy instead of velocity writing

$$dN = N_0 \frac{1}{2\pi kT} e^{-\frac{mw^2}{2kT}} d\left(\frac{m}{2} w^2\right) \quad (8.22)$$

there would have been no maximum. The distribution of density over the energy axis decreases continually with increasing energy.

to this statepoint represents the velocity of the particular molecule in magnitude and direction. In the earlier discussion it was assumed that the directions of the velocities were uniformly distributed and that all the molecules moved with the same velocity, so that all the statepoints fell on the surface of a single sphere. Now, however, the statepoints will be distributed through space with a density equal to

$$N_0 \left( \frac{m}{2\pi kT} \right)^{\frac{3}{2}} e^{-\frac{mv^2}{2kT}}$$

This density is greatest at the origin and decreases outward according to the much discussed exponential law. If a velocity is designated by its magnitude,

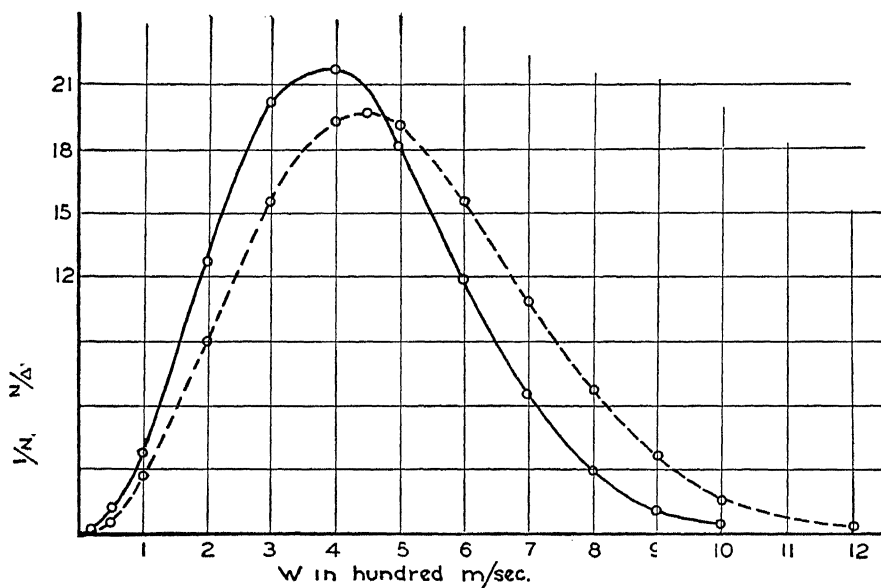


FIG. 14. Velocity Distributions for Oxygen Molecules at  $T = 273^\circ\text{K}$  (full line) and  $T = 373^\circ\text{K}$  (broken line).

$w$ , and its direction ( $\frac{1}{2}\pi - \vartheta =$  geographical latitude,  $\varphi =$  geographical longitude), instead of its components,  $\xi, \eta, \zeta$ , the size of the volume element is  $w^2 dw \sin \vartheta d\vartheta d\varphi$ . Then the number of molecules having velocities of magnitude between  $w$  and  $w + dw$ , and directions between  $\vartheta$  and  $\vartheta + d\vartheta$ , and  $\varphi$  and  $\varphi + d\varphi$ , is given by

$$d_w d_\vartheta d_\varphi N = N_0 \left( \frac{m}{2\pi kT} \right)^{\frac{3}{2}} e^{-\frac{mw^2}{2kT}} w^2 dw \sin \vartheta d\vartheta d\varphi \quad (8.26)$$

The number of molecules having speeds between  $w$  and  $w + dw$ , regardless of the direction of their motion, is the number whose statepoints lie within the



spherical shell of internal radius  $w$  and thickness  $dw$ . The statepoints are uniformly distributed in this shell and since its volume is  $4\pi w^2 dw$ , the desired number of molecules is (Fig. 14)

$$d_w N = 4\pi N_0 \left( \frac{m}{2\pi kT} \right)^{\frac{3}{2}} e^{-\frac{mw^2}{2kT}} w^2 dw \quad (8.27)$$

This number is zero when  $w$  equals zero, and increases with increasing  $w$  to a maximum at

$$\frac{1}{2}mw_{mp}^2 = kT$$

Further increase in  $w$  causes a decrease in the fraction of the molecules with speed between  $w$  and  $w + dw$ , this decrease eventually approximating the type of an exponential decrease. The mathematical reason for the presence of the maximum is, as in the two dimensional case, that although the density of state points continually decreases upon moving away from the origin, the volume of the spherical shell continually increases. Physically the last statement means that large velocities may be formed from more combinations of components than small. This again merely corresponds to the geometrical statement that there are more volume elements in the large shell, for each element of volume stands for a definite combination of the components  $\xi$ ,  $\eta$ ,  $\zeta$ . The expression for the mean energy now takes the form

$$\frac{1}{2}m\bar{w}^2 = \frac{\int_0^{+\infty} \frac{m}{2} w^2 e^{-\frac{mw^2}{2kT}} w^2 dw}{\int_0^{+\infty} e^{-\frac{mw^2}{2kT}} w^2 dw} = kT \frac{\int_0^{+\infty} x^2 e^{-x^2} x^2 dx}{\int_0^{+\infty} e^{-x^2} x^2 dx} = \frac{3}{2}kT \quad (8.28)$$

The various values of  $\frac{1}{2}m\bar{w}^2$  and  $\frac{1}{2}mw_{mp}^2$  obtained for the different models of gases assumed, may be summarized as follows:

	$\frac{1}{2}m\bar{w}^2$	$\frac{1}{2}mw_{mp}^2$
One dimensional gas.....	$\frac{1}{2}kT$	0
Two dimensional gas.....	$\frac{2}{3}kT$	$\frac{1}{2}kT$
Three dimensional gas.....	$\frac{3}{2}kT$	$\frac{3}{2}kT$

It is seen from this table, as has already been deduced from the semi-empirical relation  $E = \frac{3}{2}RT$ , that for each new direction of motion the average energy per molecule is increased by  $\frac{1}{2}kT$ . Why this should be the case becomes obvious upon writing the equation in rectangular rather than in polar coordinates.<sup>6</sup>

It is now possible to calculate the average value of the square of the relative velocity  $\bar{w}$  (see Section 4). The average value of  $\bar{w}^2$  is <sup>7</sup>

$$\bar{w}^2 = \bar{w}_1^2 + \bar{w}_2^2 \quad (8.29)$$

<sup>6</sup> For details of these calculations, see the 2d ed. of this treatise, Vol. I, pp. 108-109.

<sup>7</sup> This follows from a direct calculation in which each value of

$$\bar{w}^2 = \bar{w}_x^2 + \bar{w}_y^2 + \bar{w}_z^2$$

is multiplied by the frequency of its occurrence.

but this result would be obtained if the velocities of the molecules of types 1 and 2 were perpendicular (law of Pythagoras applied to the addition of vectors). Therefore, the average angle between  $w_1$  and  $w_2$  may be taken to be  $90^\circ$ .

The average difference of the kinetic energies of the molecules after collision is obtained by squaring and subtracting the formulas (4.1) and (4.2) (the energy due to the components of velocity perpendicular to the line of centers, which are not affected by the collisions, is added to the result); thus,

$$= \left( 1 - \frac{8m_1m_2}{(m_1 + m_2)^2} \right) \left( \frac{n}{2} \right) + 4 \frac{m_1m_2(m_1 - m_2)}{(m_1 + m_2)^2} \frac{w_{1z}^0 w_{2z}^0}{2} \quad (8.30)$$

Now the average value of the product of the components along a given line (in this case the line of centers) vanishes if, on the average, the velocities are perpendicular to each other. Therefore, the last term of the above relation is zero. Since the first parenthesis is less than unity, the energy difference between the two molecules after collision is on the average less than it was before collision. In a mixture of gases, therefore, the energies of the constituents are equalized. From this it may be concluded that when gases are placed in contact their energies finally become equal and it follows from this that the kinetic energies of all gases must be the same function of the temperature. Here again merely the constancy of the  $pV$  product in the column has been stipulated.

(9) **The Experimental Proof of Maxwell's Law:**<sup>1</sup> Qualitatively, Maxwell's law states that the molecules of a gas do not all move with the same speed and that an increase in the temperature of the gas causes an increase in the number of molecules possessing high speeds. Quantitatively, the law specifies the exact form of the distribution curve at each temperature.

On the experimental side, the distribution of a gas in a field of force shows that all molecules do not possess the same speed, since, according to the barometric formula, the molecules are sorted out by the gravitational field into a kind of velocity spectrum. Similarly, the laws of vapor pressure may be cited as proof of the distribution law in this way. In order to pass from the liquid to the vapor phase a molecule must have sufficient velocity to overcome the attractive forces holding the liquid together. These forces are evidenced by the latent heat of evaporation which is analogous to the potential energy,  $mgx$ , appearing in the barometric formula. If all the molecules of a liquid had the same velocity, none could evaporate at low temperatures. If the temperature of such a liquid were increased a point would finally be reached at which the liquid would suddenly vaporize.<sup>2</sup> This temperature would be

<sup>1</sup> J. F. Andrews, *Science Progress*, 23, 118 (1928).

<sup>2</sup> This is not quite correct, as the molecules in the liquid move at different angles toward the surface.

independent of the pressure; above it, the substance could exist only as a gas and below it only as a liquid or solid with zero vapor pressure. The experimental fact that liquids and solids can evaporate at all temperatures shows that some of the condensed molecules must have sufficient velocity to escape into the vapor phase. Further, the fact that the vapor pressure increases with the temperature shows that increase in temperature increases the number of high speed molecules. It will be seen later that the exact form of the vapor pressure-temperature curve is determined by Maxwell's law.

A study of the width of spectral lines gives further evidence for the statements of the distribution law. It may be assumed that the light emitted from a radiating atom is very nearly monochromatic. The light emitted from a large number of atoms, however, will not be monochromatic due to the motion

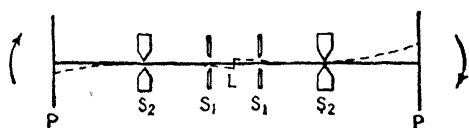


FIG. 15.

of the emitting atoms (Doppler effect). Thus, if at the instant of emission the atom is moving toward the observer, the apparent wave length is slightly less than that emitted by a stationary atom. The different motions of

the emitting atoms therefore cause a slight broadening of the line as observed by spectroscopic measurements. It has been shown<sup>3</sup> that the experimental facts are in agreement with the predictions of Maxwell's law.

The first direct measurement of molecular velocities was obtained by Stern.<sup>4</sup> His apparatus is shown diagrammatically in Fig. 15.  $L$  represents a thin platinum wire shown end on in the figure. This wire is coated with silver which upon heating to 600–700°C evaporates, the silver atoms moving off radially from the wire in the plane of the figure. The apparatus is evacuated to such a degree that the collisions between the silver atoms are negligible. Therefore the atoms move in straight lines from the wire.  $S_1$  and  $S_2$  are slits which select a ray of silver atoms of a particular direction among all evaporating from the wire. The ray of atoms after passing through the slits is condensed on the receiver  $P$  in the form of a narrow strip, just as a light source placed at  $L$  would produce a fine band on a photographic plate at  $P$ . In order to measure the speed of the silver atoms the whole apparatus is rotated about  $L$  as an axis. The silver atoms may now be regarded as being shot from the stationary wire at a moving target, since the linear velocity of the periphery of the wire  $L$  is small compared to that of the plate  $P$ . The atoms will therefore be deposited on the plate at a point slightly behind the previous point as shown by the dotted line of the diagram. In the actual experiment Stern rotated the apparatus first in one direction and then in the other, obtaining two lines each deflected from the center by the same amount but in opposite direc-

<sup>3</sup> Rayleigh, *Phil. Mag.*, 27, 298 (1889); A. A. Michelson, *ibid.*, 34, 280 (1892); H. Buisson and C. Fabry, *J. phys. rad.*, 2, 442 (1912).

<sup>4</sup> O. Stern, *Z. Physik*, 2, 49 (1920); 3, 417 (1920).

tions (Fig. 16). From this displacement, the speed of rotation and the dimensions of the apparatus, the average velocity of the silver atoms was calculated to be from 643 to 675 m/sec. The value to be expected from the theory was 672 m/sec (see Equation [35.17]).

Costa, Smyth, and Compton<sup>5</sup> have attempted a direct experimental proof of the quantitative statement of Maxwell's law. The essential parts of their apparatus are shown in Fig. 17.  $S_1$  and  $S_2$  are slits used to define a beam of molecules (see Section 25);  $D_1$  and  $D_2$  are discs slotted at the rim in the manner of cog-wheels. These discs are mounted on the common axis  $A$  in such a manner that they can be rotated at a high speed (500 to 6,000 rpm), the slots in  $D_1$  and  $D_2$  being exactly in line. At  $R$  is placed a sensitive radiometer which by its angular deflection, measures the intensity or number of molecules of the beam. The whole apparatus is placed in a highly evacuated chamber. If an experiment is made with the discs stationary and in such a position that one of the slots is opposite the slits, the radiometer deflection is a measure of the total number of molecules leaving slit  $S_1$  in the direction of  $S_2$ , since there is no obstruction offered to their motion. In the actual measurements the discs are rapidly rotated in order to sort out the molecules possessing a given speed. The mechanism of the separation is as follows. Consider a molecule leaving the slit  $S_1$  with velocity  $w$  and passing through a slot in  $D_1$ . It can only pass through a slot in  $D_2$  and be recorded

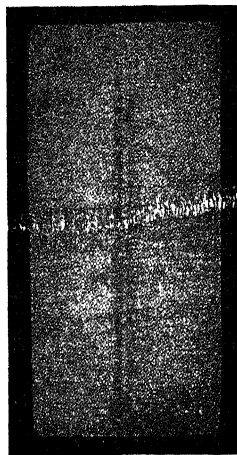


FIG. 16.

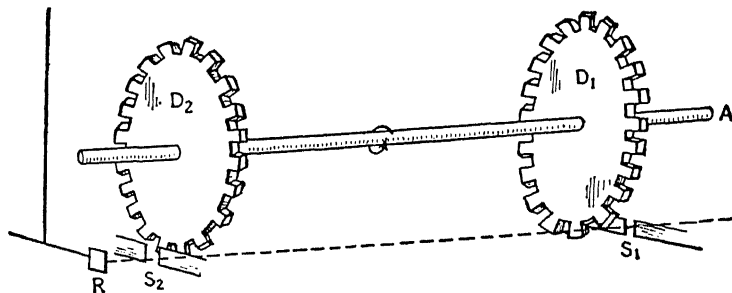


FIG. 17.

by the radiometer if the time required for the traversal of the distance between the discs equals some multiple of the time required for  $D_2$  to turn over until the next slot is in the path of the beam. That is if

$$\frac{d}{w} = n \frac{2\pi r}{a \omega} \quad \text{or} \quad nw = \frac{a d \omega}{2\pi} \quad (9.1)$$

<sup>5</sup> J. L. Costa, H. D. Smyth, and K. T. Compton, *Phys. Rev.*, 30, 349 (1927).

where  $r$  is the radius of the discs,  $d$  the distance between them,  $a$  the number of slots in each disc,  $\omega$  the angular velocity of the discs and  $n$  a small integer. The deflection of the radiometer at a rotatory speed  $\omega$  is therefore a measure of the number of molecules in the beam with a velocity approximately equal

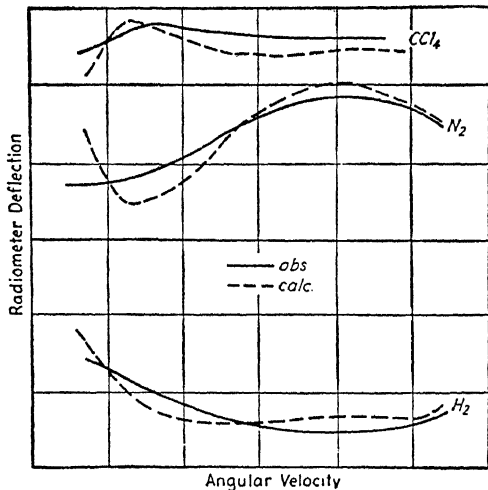


FIG. 18.

to  $w$  or a submultiple thereof. Thus, the function of the discs is analogous to that of a grating in spectroscopy in that they separate the molecules into a velocity spectrum. The lack of definition of the speeds of the selected molecules is caused by the finite width of the slots. The multiplicity of the selected velocities is analogous to the second and higher orders of spectra obtained from a grating. Thus, all the molecules passing through a given slot in  $D_1$  will miss the opposite slot in  $D_2$  due to the rotation of the discs. Those molecules, however, which have a speed  $w = ad\omega/2\pi$  ( $n = 1$ )

will pass through the next slot in  $D_2$ ; those molecules having a speed  $w = \frac{1}{2}(ad\omega/2\pi)$ , i.e.,  $n = 2$ , will pass through the third slot in  $D_2$  counted from the slot opposite the one in  $D_1$  through which the molecules entered.

Experiments were made with hydrogen, nitrogen and carbon tetrachloride. In Fig. 18 the radiometer deflection is plotted against the angular velocity of the discs. The solid lines are the results obtained by experiment and the dotted curves show the effect calculated from Maxwell's law. Although the experimental results follow the general shape of the calculated curve, it is apparent that the check is not as good as might be desired. The experimental error, however, is large enough to account for the deviations from the theoretical values. A similar experiment has been performed by Eldridge<sup>6</sup> using a beam of cadmium atoms. He also checked Maxwell's law to within his experimental error.<sup>7</sup> A considerable increase in resolving power was introduced by Zartman<sup>8</sup> and Ko.<sup>9</sup> A flat cylinder of 10 in. diameter was rotated about its axis (which is horizontal) at a rate of 30,000 rpm. In its mantle there was a narrow slit, parallel to the axis, through which a beam of molecules passed at the moment at which the slit in the rotating cylinder was opposite a fixed, collimating slit. The molecules, after entering the rotating cylinder, condensed

<sup>6</sup> J. A. Eldridge, *ibid.*, **30**, 931 (1927).

<sup>7</sup> Cf. also J. Tykocinski-Tykociner, *J. Opt. Soc. Am.*, **14**, 423 (1927).

<sup>8</sup> I. F. Zartman, *Phys. Rev.*, **37**, 383 (1931).

<sup>9</sup> Cheng Chuan Ko, *J. Franklin Inst.*, **217**, 173 (1934).

on a glass plate situated on the inside of the mantle, diametrically opposite the slit. The place where they hit depended on their speed, as in Stern's experiment. The authors used a bismuth beam, but the theoretical interpretation of their results was complicated by the presence of  $\text{Bi}_2$  and  $\text{Bi}_3$  besides  $\text{Bi}$ .

A particularly direct experiment was performed by Estermann, Simpson and Stern,<sup>10</sup> who measured the deflection of a horizontal beam of cesium atoms by gravity. The deflection of a beam of length  $L$  (about 200 cm was chosen) is given by  $\frac{1}{2}g(L/w)^2$ . The experiment is not yet sufficiently exact for a confirmation of Maxwell's law.

A beam of electrically charged particles is much simpler to produce and measure than a beam of neutral molecules. It has been used to confirm Maxwell's law for electrons and positive ions with much greater accuracy than was obtained in the experiments outlined above. Richardson<sup>11</sup> and his coworkers have shown that the velocities of the electrons and positive ions emitted from hot bodies are distributed according to Maxwell's law at the temperature of the emitting body.

One of the first experiments to show directly that the molecules of a gas possess high velocities is due to Cantor.<sup>12</sup> If one side of a copper plate is protected with glass and the whole hung in an atmosphere of chlorine, the side covered with glass experiences the full pressure  $p = RT/V$ . The pressure on the exposed side is smaller because some of the molecules of chlorine which form a solid compound with copper do not rebound elastically and therefore the momentum imparted by each of these molecules is only  $mw$  instead of  $2mw$ . This side therefore receives less than the normal amount of momentum. The excess pressure can readily be measured by mounting two such plates as vanes on an axis. From this value and the increase in the weight of the plate it is possible to calculate the number of molecules which do not rebound and their average momentum (velocity). Assuming that a molecule must have a minimum velocity to combine with the copper, the determination of the way in which the quantities mentioned above vary with temperature would lead to an experimental determination of the distribution law.<sup>13</sup>

A model of the molecular motion in gases which is suitable for educational purposes has been developed by Minneart.<sup>14</sup> A piece of plane plate glass 70 cm square is laid flat on a table. The molecules are represented by steel ball bearings about 8 mm in diameter, and their motion is limited by a frame 40 cm square made of wood about 2 cm thick, the frame taking the part of the walls of the containing vessel. If the frame is now moved across the glass plate so

<sup>10</sup> I. Estermann, O. C. Simpson and O. Stern, *Phys. Rev.*, **71**, 278 (1947).

<sup>11</sup> O. W. Richardson, *The Emission of Electricity from Hot Bodies* (New York: Longmans, Green and Co., 1921), p. 154 ff. and p. 206 ff.

<sup>12</sup> M. Cantor, *Wied. Ann.*, **62**, 482 (1897).

<sup>13</sup> A. Predvoditelev, *Z. Physik*, **46**, 406 (1928); cf. also L. Frommer and M. Polanyi, *Z. physik Chem.*, **137A**, 201 (1928).

<sup>14</sup> M. Minneart, *Z. physik. chem.* ~~B 227, 111 (1919)~~ **122**, 80 (1919) Improvement by T. Wulf, *ibid.*, **34**, 5 (1921).

that each point describes a circle about 6 cm in diameter, the balls are set in motion and exchange the motion by collisions until a steady state is reached. In this case the motion of the frame corresponds to collisions of the molecules with a hot containing wall. The free path and number of collisions per second (see below) can be estimated in this manner and it can be observed how each ball moves in all directions in course of time and also changes the magnitude of its velocity. Moreover, the irregular nature of the path can be followed. In order to follow the course of a single ball, it is desirable to have one of the same mass but of different color, as for example, brass. If a smaller steel ball is added, it is seen to have a much greater velocity than the others.

If one side of the glass plate is blocked up higher than the other, the movement of the frame produces a barometric distribution of the balls since most of them stay in the lower portion although some are being continually thrown back into the upper region. If a mixture of balls of different weight is used the lighter ones are seen to spend more time in the upper part. A contrivance may be made out of a wooden border and tin strips which, when suddenly put into the frame while the balls are in motion, will separate them into horizontal strips. The distribution may then be counted. Furthermore, the interior of the frame may be divided into two parts, one of which contains large balls, the other small. If there is a hole in the dividing wall about 3 cm across (the top of the wall being held together by a tin strip), the process of diffusion may be illustrated (Section 42).

(10) **Extension of Maxwell's Law to the Maxwell-Boltzmann Law:** Conversely to the procedure of Section 7, the distribution in space of a gas in a field of force which is independent of the time and which has a potential, can be deduced from the law governing the distribution of velocities. A reference point is arbitrarily selected in the space to be considered and the symbol  $\epsilon_p$  is used to designate the work required to move a molecule from the reference point to any given point in the field. That is, the potential at the given point is calculated by arbitrarily setting the potential at the reference point equal to zero. Let  $N_0$  be the number of molecules per cubic centimeter at the reference point. Then the "Maxwell-Boltzmann distribution,"<sup>1</sup>

$$dN = N_0 \left( \frac{m}{2\pi kT} \right)^{\frac{3}{2}} e^{-\left( \epsilon_p + \frac{m}{2} \xi^2 + \frac{m}{2} \eta^2 + \frac{m}{2} \zeta^2 \right) / kT} d\xi d\eta d\zeta \quad (10.1)$$

holds at the given point. This relation states that the Maxwell distribution of velocities (and also the isotropic distribution of directions of velocities) holds at every point in the space but that the total density of the molecules at the point is to be taken as

$$N = N_0 e^{-\frac{\epsilon_p}{kT}} \quad (10.2)$$

The content of formula (10.1) may also be expressed by the statement that the exponent is proportional to the sum of the potential energy ( $\epsilon_p$ ) and the kinetic

<sup>1</sup> L. Boltzmann, *Wien. Ber.*, 58, 517 (1868); 63, 397 (1871).

energy ( $\frac{1}{2}m\xi^2 + \frac{1}{2}m\eta^2 + \frac{1}{2}m\zeta^2$ ), instead of to the kinetic energy alone as was formerly the case.

This formula is valid for all fields of force, even those in which the change in the potential is large upon traversing a distance of the order of magnitude of the molecular diameter.<sup>2</sup>

The derivation is merely the reverse of the process used in Section (7). As an especially simple example consider a vessel separated into two parts by a dividing wall. No forces act within the two halves of the vessel, but in order to carry a molecule from left to right through the wall, a definite amount of work  $\epsilon_p$  is required. For instance, the molecules may be supposed to be electrically charged and the dividing wall to consist of two wire gauzes close together and connected to form a condenser. The same temperature and distribution of velocities then prevails on each side of the dividing wall. On the left hand side, however, the density is greater than that on the right by an amount given by the relation

$$c_r = c_l e^{-\frac{\epsilon_p}{kT}} \quad (10.3)$$

Without going into particulars, this formula, as well as the fact of temperature constancy can be deduced, according to Jäger, merely from the condition that, in the stationary state, as many molecules pass across from left to right as in the opposite direction, and that the net heat exchange across the wall is zero.

There is still in this argument an apparent difficulty which has also been explained by Jäger. Consider a vessel separated into three parts by two dividing walls of the kind described above (Fig. 19). Then an amount of work equal to  $\epsilon_p$  must be done on a molecule to transport it from II to either I or III. Consider now a molecule in I with an  $x$ -component of velocity equal to  $\xi$ , the  $x$ -axis being taken from I to II perpendicular to the dividing wall. Upon crossing the left wall  $\xi$  is increased according to the equation

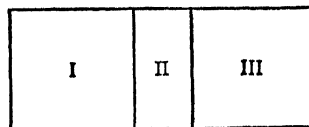


FIG. 19.

$$\frac{1}{2}m\xi_{II}^2 = \xi_1^2 + \quad (10.4)$$

It traverses II with this higher velocity but, upon passing the right hand wall, it loses kinetic energy to the amount  $\epsilon_p$ , since this energy must be given up as work to effect the passage. It then moves in compartment III with its original velocity:

$$\frac{1}{2}m\xi_{III}^2 = \frac{1}{2}m\xi_{II}^2 - \epsilon_p = \frac{1}{2}m\xi_1^2 \quad (10.5)$$

From this it might be argued that since the molecule has a greater velocity in II than in either I or III, the *density* in II must be *less* than in I and III because the molecule requires less time to traverse a given path in II than in either I or III and hence in II it does not remain as long in a given volume as

<sup>2</sup> G. Jäger, *ibid.*, 112, 307 (1903); 113, 1289 (1904).



it does in the same volume of I and III. A similar effect is noticed when men walking single file start to run upon passing some fixed point; the distance between the running men is greater than that between the men who are still walking.

On the other hand, the Boltzmann law requires that the *density* be *greatest* in compartment II.

The explanation of this apparent contradiction results upon taking into account those molecules which lose so much energy by collisions in II that  $\frac{1}{2}m\bar{v}_{II}^2 < \epsilon_p$ . These molecules have not enough energy to effect a passage through either of the dividing walls, for upon colliding with either of them they will penetrate to a certain depth and then be returned into II. They are then "reflected" back and forth between the two dividing walls and accordingly spend a large proportion of their time in compartment II. They cannot get out of this compartment until some collision has given them sufficient energy to make the passage. Even then they can get out only if they do not lose the energy again in another collision before reaching the dividing wall.

This retention of molecules in II is therefore the cause of the greater density existing in II, although, from the previous discussion, the density of those which pass completely through compartment II without collision is smaller than the density in I and III. It must be particularly noted, however, that the density of this single class of molecules is greater by the factor  $e^{\epsilon_p/kT}$  than the density of molecules of *equal* kinetic energy in compartments I and III. Those molecules which are retained in II due to a loss of energy by collision have small velocities,  $\frac{1}{2}m\bar{v}_{II}^2 < \epsilon_p$ , while the molecules which have just entered this compartment have a component of velocity in the  $x$ -direction  $\frac{1}{2}m\bar{v}_{II}^2 > \epsilon_p$ . Both of these classes of molecules participate in the Maxwell distribution which must prevail throughout the gas; that is, the retained molecules contribute the slow velocities and the entering molecules the high velocities with the result that, taken as a whole, the distribution of velocities is represented by Maxwell's law.

(11) **The Number of Collisions. The Mean Free Path:** (*a*) *Preliminary Treatment:* Up to this point the occurrence of collisions has been used to explain the equalization of velocities but, as yet, nothing has been said in regard to the number of the collisions. To evaluate this quantity it will first be assumed that the molecules are rigid spheres which are without influence upon each other except at the instant of collision. It is further postulated that the gas is sufficiently attenuated to permit the assumption that during the collision of two molecules the chance of a third molecule being close enough to affect the process of collision is negligibly small. Consider a mixture of two gases which have the molecular diameters  $d_1$  and  $d_2$ . A collision between two different molecules results if their centers approach to within a distance  $(d_1 + d_2)/2$ , corresponding to contact of their spherical surfaces (Fig. 20). This may also be expressed by supposing spheres of radius  $(d_1 + d_2)/2$  circumscribed about the molecules of the first kind and stating that a collision takes place when the center of a molecule of the second kind touches one of these spheres. Fol-

lowing Clausius' <sup>1</sup> treatment, the problem will be simplified by assuming that all the molecules of type I are held stationary and that there is only a single molecule of the type II present. This molecule is permitted to move with the velocity  $w$ . It is now necessary to determine the probability that this molecule will collide with one of the stationary molecules while traversing the interval  $\Delta x$ . Consider a cylinder with base equal 1 cm<sup>2</sup> and height  $\Delta x$ . There are  $N_1 \Delta x$  molecules of type I in this cylinder, where  $N_1$  denotes the number of molecules of type I per cc. The single molecule of type II is now supposed to move toward the base of this cylinder, which offers to the molecule a surface of 1 cm<sup>2</sup>, part of which, however, is covered by the cross-section of  $N_1 \Delta x$  spheres of radius  $(d_1 + d_2)/2$  circumscribed about the molecules of type I. The covered portion of the surface equals  $N_1 \Delta x \pi [(d_1 + d_2)/2]^2$ . If, upon traversing the cylinder, the center of the moving molecule comes in contact with this covered portion, a collision has taken place, but if, throughout the passage through the cylinder, the center of this molecule never falls within the spheres surrounding the molecules of type I, molecule II crosses the interval  $\Delta x$  undisturbed. It is essential for the validity of the following reasoning that the moving molecule is not "aiming for" any other molecule.

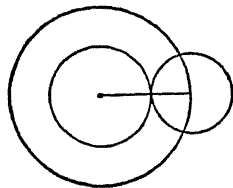


FIG. 20.

The problem is now entirely analogous to the following. A marksman shoots a number of shots toward a target without taking aim at any particular point on the target. Since, on the average, the bullets that hit the target will be uniformly distributed throughout its area, the fraction of bullets hitting the bull's-eye will equal the fraction of the total area of the target occupied by the bull's-eye.

Similarly, to return to the problem in hand, the probability that the moving molecule will collide with a stationary one is

$$N_1 \pi \left( \frac{d_1 + d_2}{2} \right)^2 \Delta x \quad \text{or} \quad \frac{\Delta x}{\Lambda}$$

where the "mean free path,"  $\Lambda$ , is defined by the equation

$$\Lambda = \frac{1}{N_1 \pi \left( \frac{d_1 + d_2}{2} \right)^2} \quad (11.1)$$

or, in the case of a single gas,

$$\Lambda = \frac{1}{N \pi d^2} \quad (11.2)$$

Thus, in a layer of thickness  $\Lambda$  and surface 1 cm, the "absorbing area" (Lenard), i.e., the sum of the surfaces presented to the moving molecule disregarding

<sup>1</sup> R. Clausius, *Pogg. Ann.*, 105, 239 (1858).

the effect of overlapping, is equal to

$$\Lambda N_1 \pi \left( \frac{d_1 + d_2}{2} \right)^2 \quad 1 \text{ cm}^2 \quad (11.3)$$

In other words, aside from overlapping, the area in a layer of thickness  $\Lambda$  appears to the moving molecule as if it were completely covered.

The reason for the choice of the name "mean free path" for this interval will be made evident by the following considerations. Suppose a ray of molecules of type II, all having approximately the same direction of motion and equal velocities, is shot into gas I. Then more and more of the molecules II will collide with molecules I and be deflected from the path of the ray. The probability that a molecule will experience a collision upon moving over the distance  $dx$ , is, from the above,  $dx/\Lambda$ . The fraction of the molecules which are deflected from the ray during this interval is accordingly

$$\frac{dN_2}{N_2} = - \frac{dx}{\Lambda} \quad (11.4)$$

Upon integration this gives the number of molecules still present in the ray after passing over the length of path  $x$ , viz.,

$$N_2 = N_{02} e^{-x/\Lambda} \quad (11.5)$$

Therefore, this number of molecules decreases in a geometric progression. Hence the probability that a molecule can move over the distance  $x$  without taking part in a collision is  $e^{-x/\Lambda}$ , and is thereby independent of the point at which the last collision has taken place, since it has not been assumed in the deduction that the point  $x = 0$  must coincide with the point of the last collision,  $x = 0$  being an arbitrarily selected point.<sup>2</sup> The mean value of the distance through which a molecule moves without colliding is given by

$$\int_0^\infty \frac{x e^{-x/\Lambda} dx}{e^{-x/\Lambda} dx} = \Lambda \quad (11.6)$$

from which follows the name of mean free path.

The probability that a molecule will collide at least once,<sup>3</sup> on traversing the distance  $x$  is equal to  $1 - e^{-x/\Lambda}$ .

(b) *Direct Experimental Measurements:* Equation (11.5) affords a direct experimental test of the demonstration and also a method of measuring the mean free path. The simplest way to perform the experiment is with electrically charged particles since, in this case, the charge transferred affords a

<sup>2</sup> For the explanation of a misunderstanding in this connection see R. Clausius, *Wied. Ann.*, 10, 92 (1880), and *Mech. Wärmetheorie* (Brunswick: 1891), III, p. 204.

<sup>3</sup> A number of other problems may be treated as corollaries of this. For example, the probability that a molecule will collide for the first time on a given path within the interval between  $x$  and  $x + dx$  is equal to the product of the probability that it will not collide between 0 and  $x$  into the probability that it will collide in  $dx$ , therefore equalling  $e^{-x/\Lambda} dx/\Lambda$ .

ready means of determining the number of particles. Measurements of this kind were first made by Lenard using electrons.<sup>3</sup> He found that the number of particles in a ray of electrons passing through a gas changes according to the relation

$$N = N_0 e^{-\alpha x} \quad (11.7)$$

According to (11.5), the coefficient of absorption,  $\alpha$ , equals  $1/\Lambda$ , that is, it is equal to the sum of the absorbing areas contained in 1 cc., namely,

$$\left[ cN_A \pi \left( \frac{d_1 + d_2}{2} \right)^2 \right] \quad (11.8)$$

if  $x$  is measured in centimeters. W. Wien<sup>4</sup> has, moreover, performed similar experiments with canal rays. In this case, however, all the collisions are not of the same kind since a fraction  $\alpha_1$  of the collisions may excite the emission of light, a fraction  $\alpha_2$  may ionize the molecule and so forth. Then the molecule must move  $1/\alpha_1$  times as far, in order to be excited to luminescence, than if each collision acted in this particular manner. There is then a special mean free path for the emission of light  $\Lambda_1 = \Lambda/\alpha_1$  and the number of molecules emitting in the interval  $dx$  is

$$\frac{dN}{N} = \frac{dx}{\Lambda_1}, \text{ etc.} \quad (11.9)$$

In some cases two opposed processes can be caused by collisions. Thus, there are present in a canal ray  $N_1$  neutral molecules, with mean free path equal to  $\Lambda_1$ , and  $N_2$  ions whose mean free path equals  $\Lambda_2$ . When the neutral molecules of the ray collide with the molecules of the surrounding gas, ionization of the gas molecules takes place. On the other hand, these ions are neutralized by collisions with the neutral molecules. Such phenomena are represented by the following formula:

$$dN_1 = -dN_2 = -N_1 \frac{dx}{\Lambda_1} + N_2 \frac{dx}{\Lambda_2} \quad (11.10)$$

The first term on the right designates the decrease in number of neutral molecules due to ionization and the second term represents the increase due to neutralization. In the stationary state  $dN_1 = -dN_2 = 0$ , and therefore the equilibrium concentrations are proportional to the free paths:

$$\frac{N_1^0}{N_2^0} = \frac{\Lambda_1}{\Lambda_2} \quad (11.11)$$

<sup>3</sup> P. Lenard, *Ann. Physik*, **12**, 714 (1903), especially p. 737. Electrons of a cathode ray behave like the molecules of a gas in that they move in straight lines without "aiming." They are readily detectable by their electric charge and energy.

<sup>4</sup> *Ibid.*, **39**, 519 (1912); **70**, 1 (1923).

For the investigation of neutral molecules, molecular rays have to be used. This was first done by Born<sup>5</sup> and Bielz.<sup>6</sup> They allowed a ray of evaporated silver atoms to enter air at a very low pressure and measured the decrease in the number of the silver atoms by measuring the amount precipitated on a glass plate in a definite time for different distances of the plate along the ray. The other methods of producing and detecting molecular rays, as described in Section 25, have also been used.<sup>7</sup>

It is possible to work in either one of two ways. First the receiver can be displaced by the distance  $d$ . If the intensities of the beam measured in the two cases are  $I_1$  and  $I_2$ , then

$$\alpha = \frac{1}{d} \ln \frac{I_1}{I_2} \quad (11.12)$$

On the other hand, the position of the receiver can be fixed and the pressure of the scattering gas changed. According to (11.8),  $\alpha$  is proportional to  $N$ , i.e., to the pressure. Therefore

$$D(\alpha_2 - \alpha_1) = \alpha_1 \left( \frac{p_2}{p_1} - 1 \right) D = \ln \frac{I_1}{I_2} \quad (11.13)$$

where  $D$  is the whole distance the beam traverses in the scattering gas. The latter method has the advantage that no moving parts in the vacuum are necessary, but the disadvantage is that  $D$  might not be accurately known.

Values of the mean free path can be obtained indirectly from measurements of viscosity; see Section 21.

(c) *A More Exact Discussion:* It has been assumed up to this point that the molecules with which those of the ray collide are practically stationary, only the molecules of the ray being in motion. This assumption is justifiable for the case of electrons and canal rays. Upon considering ordinary gas molecules, however, the velocities of each of the participants in the collisions are of the same order of magnitude. This means that  $\sqrt{\bar{w}^2}$  is the mean *relative* velocity of the molecules of both classes. If a Maxwellian distribution prevails it is seen from Equation (8.37) that

$$\sqrt{\bar{w}^2} = \sqrt{\bar{w}^2 + \bar{w}'^2}$$

<sup>5</sup> M. Born and E. Bormann, *Physik. Z.*, **21**, 578 (1920).

<sup>6</sup> *Z. Physik*, **32**, 81 (1925).

<sup>7</sup> H. Kerschbaum, *Ann. Physik*, **2**, 213 (1929); E. G. Lunn and F. R. Bichowsky, *Phys. Rev.*, **35**, 563, 671 (1930); I. Amdur and H. Pearlman, *J. Chem. Phys.*, **8**, 7 (1940); I. Amdur, *ibid.*, **11**, 157 (1943); for H atoms. R. G. J. Fraser and L. F. Broadway, *Proc. Roy. Soc.*, **A**, **141**, 626 (1933); L. F. Broadway, *ibid.*, p. 634; W. H. Mais, *Phys. Rev.*, **45**, 773 (1934); S. Rosin and I. I. Rabi, *ibid.*, **47**, 645, 798 (1935); **48**, 373 (1935); I. Estermann, S. N. Foner, and O. Stern, *ibid.*, **71**, 250 (1947); for alkali atoms. F. Knauer and O. Stern, *Z. Physik*, **53**, 766 (1929); I. Estermann and O. Stern, *ibid.*, **85**, 135 (1933); F. Knauer, *ibid.*, **80**, 80 (1933); **90**, 559 (1934); R. Zabel, *Phys. Rev.*, **44**, 53 (1933); **46**, 411 (1934); J. A. Eldridge, *ibid.*, **49**, 411 (1936); for permanent gases.

where  $\overline{w^2}$  is the mean square velocity of the molecules receiving the collision. If all the molecules are the same  $\overline{w'^2} = \overline{w^2}$  and  $\sqrt{\overline{w'^2}} = \sqrt{2}\overline{w}$ .

It is seen from this that  $\overline{w} > w$ , i.e., the receiving molecules act as if they were, on the average, moving toward the colliding molecules. On account of this, the number of collisions is increased in the ratio

$$\sqrt{\frac{\overline{w'^2}}{w^2}} = \sqrt{1 + \frac{\overline{w'^2}}{w^2}} \quad (11.14)$$

The deduction is not yet entirely rigorous because in a group of molecules whose velocities are distributed according to Maxwell's law, there are some which have especially high velocities. The absolute velocities of these are less different from their velocities relative to an average molecule than is the case for slow molecules, because the other molecules are moving slowly in comparison to them. On account of this, the free path of a given molecule depends to a certain extent upon the velocity of that molecule and, in fact, increases with its velocity. Upon taking an appropriate average, there is obtained for the mean free path of a molecule of type I in a mixture of two different kinds of molecules,

$$\frac{1}{\Lambda} = \left\{ \pi \sqrt{2} N_1 d_1^2 + \pi N_2 \left( \frac{d_1 + d_2}{2} \right)^2 \sqrt{\frac{m_1 + m_2}{m_2}} \right\} \frac{1}{v} \quad (11.15)$$

Here the first summand takes into account the collisions with other molecules of type I and the second summand collisions with molecules of type II. It is seen that the mean free path is inversely proportional to the density as must follow from the discussion of the foregoing paragraphs in which the number of collisions was shown to be proportional to the density.<sup>8</sup>

A comparison of the case of a molecule moving among others of its own kind ( $d_1 = d_2$ ), with the case in which a dimensionless molecule ( $d_1 = 0$ ) (electron) moves among ordinary molecules ( $d_2$ ), shows that the mean free path in the latter case is four times as large as the mean free path in the former case, provided that the molecules of diameter  $d_2$  act like rigid spheres to the point molecule.

The number of collisions made by a molecule of type I with molecules of type II while the former traverses a distance of 1 cm is

$$\frac{N_2}{v} \pi \left( \frac{d_1 + d_2}{2} \right)^2 \sqrt{\frac{m_1 + m_2}{m_2}}$$

<sup>8</sup> On the other hand, the average distance between the molecules is inversely proportional to the cube root of the density  $1/\sqrt[3]{N/v}$ . This latter magnitude is proportional to a kind of geometric mean of the mean free path and the square of the molecular diameter

$$1/\sqrt[3]{N/v} \propto \sqrt[3]{\Lambda d^2}.$$

From this relation there is obtained for the number of collisions per molecule of type I per second (with  $\bar{w} = 2\sqrt{2kT/\pi m_1}$ ),

$$2\sqrt{2\pi} \frac{N_2}{v} \left( \frac{d_1 + d_2}{2} \right)^2 \sqrt{\frac{m_1 + m_2}{m_1 m_2} kT}$$

Since there are altogether  $N_1/v$  molecules of this type per cubic centimeter, and since they move independently of each other, each experiences on the average the same number of collisions in equal intervals of time. Therefore the total number of collisions between molecules of type I and molecules of type II per second per cubic centimeter equals

$$2\sqrt{2\pi} \frac{N_1 N_2}{v^2} \left( \frac{d_1 + d_2}{2} \right)^2 \sqrt{\frac{m_1 + m_2}{m_1 m_2} kT} \quad (11.16)$$

This quantity is seen to be proportional to the product of the densities of the two kinds of molecules present. The number of collisions between molecules of the same kind is, (cf. Equation [8.13])

$$\frac{N^2}{v^2} d^2 \sqrt{\frac{4\pi kT}{m}} = \frac{N^2}{2v^2} |\bar{w}| \pi d^2 \quad (11.17)$$

The factor 1/2 is introduced since otherwise each collision would be counted twice, each molecule being counted once as the colliding particle and again as the receiving particle, in the same process.

To illustrate the numerical magnitude of these quantities the value of  $\Lambda$  for hydrogen may be taken. From viscosity measurements this is found to be  $1.18 \times 10^{-5}$  cm at  $0^\circ$  and normal density. The average distance between the molecules under these conditions is  $0.33 \times 10^{-6}$ . At a pressure of  $0.9 \times 10^{-2}$  mm Hg,  $\Lambda$  equals 1 cm. The mean distance between the molecules equals 1 cm at a pressure of  $2.8 \times 10^{-17}$  mm. The number of collisions experienced by a hydrogen molecule per second at one atmosphere and  $0^\circ$  is about  $1.4 \times 10^{10}$ , the total number per second per cubic centimeter being  $1.9 \times 10^{29}$ . At a pressure of  $0.9 \times 10^{-2}$  mm, there are still  $2.6 \times 10^{19}$  collisions per second per cubic centimeter. The number of collisions increases with the square root of the temperature, since it is proportional to  $w$ .

(12) **Special Types of Collisions:** The present section is devoted to the deduction of a number of equations which are useful in the study of the velocity of gaseous reactions.

(a) *Collisions with the Walls:* The first equation to be developed will give the number of collisions with the wall of the containing vessel in which the component of velocity perpendicular to the wall ( $\xi$ ) is greater than some specified value  $\xi_0$ . The number of such collisions per square centimeter per

second equals :

$$\left. \begin{aligned} \int_{\xi_0}^{\infty} \xi dN &= \frac{N_0}{v} \frac{\int_{\xi_0}^{\infty} \xi e^{-\frac{m\xi^2}{2kT}} d\xi}{\int_{-\infty}^{+\infty} e^{-\frac{m\xi^2}{2kT}} d\xi} \\ &= \frac{N_0}{v} \sqrt{\frac{2kT}{m}} \frac{\int_{\sqrt{m\xi_0^2/2kT}}^{\infty} x e^{-x^2} dx}{\int_{-\infty}^{+\infty} e^{-x^2} dx} \end{aligned} \right\} \quad (12.1)$$

where  $x$  is defined by Equation (8.4). Upon performing the indicated integrations, the desired quantity is found to be

$$\frac{N_0}{2v} \sqrt{\frac{2kT}{\pi m}} e^{-\frac{m\xi_0^2}{2kT}} \quad (12.2)$$

By an entirely similar calculation the number of collisions with the wall per square centimeter per second in which the *total* velocity of the molecule is greater than  $w_0$ , is found to be

$$\frac{N_0}{2v} \sqrt{\frac{2kT}{\pi m}} \left( 1 + \frac{mw_0^2}{2kT} \right) e^{-\frac{mw_0^2}{2kT}} \quad (12.3)$$

(b) *Collisions between Two Molecules*: The next important type of collision is one between two molecules of different types in which the *relative* velocity of the molecules is greater than some definite value  $\tilde{w}_0$ . The equation giving the number of pairs of molecules whose relative velocities lie between  $\tilde{w}$  and  $\tilde{w} + d\tilde{w}$  can easily be found. Upon introducing space polar coordinates this expression becomes

$$\begin{aligned} d_w(N_1 N_2) &= N_{01} N_{02} \left( \frac{3}{2\pi(\overline{w_1^2} + \overline{w_2^2})} \right)^3 \\ &\quad \times e^{-\frac{3}{2} \cdot \frac{\tilde{w}^2}{\overline{w_1^2} + \overline{w_2^2}}} \tilde{w}^2 d\tilde{w} \int_0^\pi \sin \vartheta d\vartheta \int_0^{2\pi} d\varphi \end{aligned} \quad (12.4)$$

If the right hand side of this expression be multiplied by  $\tilde{w}$  and by the collision area of the colliding molecules,  $\pi[(d_1 + d_2)/2]^2$ , there is obtained the number of collisions per second per cubic centimeter in which the relative velocity is between  $\tilde{w}$  and  $\tilde{w} + d\tilde{w}$ . Integration of this quantity from  $\tilde{w}_0$  to  $\infty$  gives the

<sup>1</sup> Cf. Equation (8.12) and Section 3.



number of collisions in which the relative velocity is greater than  $\tilde{w}_0$ . This is <sup>2</sup>

$$2\sqrt{2\pi} \frac{N_{01}N_{02}}{v^2} \left( \frac{d_1 + d_2}{2} \right)^2 \sqrt{\frac{m_1 + m_2}{m_1 m_2}} kT \times \left( 1 + \frac{m_1 m_2}{m_1 + m_2} \cdot \frac{\tilde{w}_0^2}{2kT} \right) e^{-\frac{m_1 m_2}{m_1 + m_2} \cdot \frac{\tilde{w}_0^2}{2kT}} \quad (12.5)$$

It can also be shown that the number of collisions in which the component of relative velocity along the line of centers is greater than  $\tilde{\xi}_0$  is

$$2\sqrt{2\pi} \frac{N_{01}N_{02}}{v^2} \left( \frac{d_1 + d_2}{2} \right)^2 \sqrt{\frac{m_1 + m_2}{m_1 m_2}} kT e^{-\frac{m_1 m_2}{m_1 + m_2} \cdot \frac{\tilde{\xi}_0^2}{2kT}} \quad (12.6)$$

A comparison of (12.6) with (12.2) and of (12.5) with (12.3) shows that, for the calculation of mutual collisions, one has to replace the mass by the effective mass, the velocity by the relative velocity and 1 cm<sup>2</sup> of the wall by four times the cross section of the molecules II per cc.

(c) *Triple Impacts*: In the theoretical treatment of reactions of higher order than the second it is necessary to know the number of multiple collisions taking place. The most important of such collisions is one in which three molecules collide nearly simultaneously; a so-called triple impact. Such a process may be defined in a number of ways but the equations resulting from the various definitions agree in the order of magnitude assigned to the number of such collisions. If it be supposed that when two molecules collide they remain in contact an infinitely short time, the probability that a third molecule shall hit the pair while in contact is naturally zero. It is therefore necessary to define a finite time during which two molecules can still be said to be in collision. A triple collision is then one in which the third molecule hits the other two while they are still "in collision." One possible definition of the time of collision is the interval in which the distance between the two molecules is less than the molecular diameter.<sup>3</sup> From this definition it follows that approximately

$$Z_{\text{III}}:Z_{\text{II}} = d:\Lambda$$

where  $Z_{\text{III}}$  and  $Z_{\text{II}}$  are the numbers of triple and double collisions per second per cubic centimeter respectively,  $d$  the diameter of the molecule and  $\Lambda$  its mean free path. Substituting for  $Z_{\text{II}}$  and  $\Lambda$  from equations (11.17) and (11.15) it is found that

$$Z_{\text{III}} = Z_{\text{II}} \frac{d}{\Lambda} = 2 \frac{N^2}{v^2} d^2 \sqrt{\frac{\pi kT}{m}} \left( \frac{d}{\pi \sqrt{2N} d^2} \right) \left\{ 2\sqrt{2\pi} \frac{N^3}{v^3} d^5 \frac{|\pi kT}{m} \right\} \quad (12.7)$$

<sup>2</sup> Cf. expression (11.16). Here again the result must be divided by 2 for collisions between identical molecules to avoid counting the same collision twice. P. Langevin and G. Roy, *Le Radium*, 10, 142 (1913).

<sup>3</sup> K. F. Herzfeld, *Z. Physik*, 8, 132 (1921).

Similar equations can be developed for triple collisions between unlike molecules but these expressions can only be valid to within the order of magnitude due to the uncertainty of the definition of a triple collision.<sup>4</sup>

(13) **The Relation Between the Mean Free Path and the Temperature:** The assumptions that have been made in the foregoing calculations lead to the conclusion that the mean free path is independent of the temperature. The indirect experimental determinations of the mean free path, however, show an increase with rising temperature. This means that the effective diameter of the molecules decreases with rising temperature.<sup>1</sup> Since the effective diameter of the molecules is found to vary with the temperature, they can no longer be regarded as rigid spheres, exerting no forces on each other except when in contact during collisions. Rather must the assumption now be made that molecules influence each other when they are comparatively far apart, but with forces which, in the light of all the experimental evidence, decrease rapidly with increasing distance. Let it be assumed, as a first approximation, that the forces are radial with spherical symmetry; that is, the force between two molecules regardless of their orientation is given by the relation  $A/r^n$ , where  $r$  is the distance between the centers. It is found from experimental data that  $n$  must be assumed to have rather large values (5 to 12) while modern theory suggests 7.

Under these circumstances the previous definition of the mean free path as that distance which a molecule can traverse without being affected by others, loses its meaning because molecules now affect each other at relatively great distances (with decreasing strength) so that a collision is no longer sharply defined. Nevertheless, it is possible to frame other more suitable definitions. One presentation, which is especially useful, is due to Sutherland,<sup>2</sup> who considers the molecules as hard spheres which exert attractive forces on one another. In this case, as before, a collision may be defined as a process in which the surface of two molecules touch, or in which the distance between the centers is  $d$ . The forces between the molecules do not change the immediate effect of the collisions, which take place exactly as in the former case of rigid, force-free spheres. The forces, however, affect the motion before and after the collision. Consider two molecules moving in such a manner that they are not aimed toward each other. They would not collide if it were not for the attractive forces. These latter, however, draw the molecules together so that a collision takes place. The effect of the forces is therefore to increase the number of collisions and thereby decrease the mean free path. The greater the molecular velocities (the greater the temperature) the smaller is this deflection, provided that the forces remain constant. Therefore, the increase in number of collisions is less at high temperatures and the mean free path is

<sup>4</sup> Cf. J. K. Syrkin, *Physik. Z.*, **24**, 236 (1923); R. C. Tolman, *Statistical Mechanics with Applications to Physics and Chemistry* (New York: Chemical Catalog Co., 1927), p. 247.

<sup>1</sup> If the molecules had a thermal expansion such as is observed in solid bodies, it would have the reverse effect.

<sup>2</sup> W. Sutherland, *Phil. Mag.*, **36**, 507 (1893).

increased. At very high temperatures the molecules move as if there were no attractions between them because their kinetic energy is so large in comparison to the potential energy of the attractive forces that their mean free path is given by Equation (11.1). The quantitative relation is <sup>3</sup>

$$\Lambda = \frac{\Lambda_\infty}{1 + \frac{T}{C}} = \Lambda_\infty \frac{T}{C + T} \quad (13.10)$$

<sup>3</sup> Consider a stationary molecule toward which another one is moving in such a manner that, disregarding for the moment the attractive forces, the nearest approach of the centers of the two molecules is  $r_0$ . The attractive force is a function of the distance alone and may be derived from a potential energy by the equation

$$F = -\frac{\partial \epsilon_p}{\partial r} \quad (13.1)$$

This potential energy  $\epsilon_p$  will be set equal to zero at  $r = \infty$ . Assume a system of polar coordinates with the stationary molecule as origin. At the beginning of the process, when the two molecules are at an infinite distance, the velocity of the moving molecule is equal to the original relative velocity  $\tilde{w}_0$  of the two particles,

$$\overline{w_0^2} = \frac{3kT}{m_1 m_2} (m_1 + m_2) = \frac{3kT}{\bar{m}} \quad (13.2)$$

The velocity  $\tilde{w}$  can be resolved into two components, one in the direction of the radius vector and another perpendicular to it,

$$\tilde{w}^2 = \left(\frac{dr}{dt}\right)^2 + r^2 \left(\frac{d\varphi}{dt}\right)^2 \quad (13.3)$$

and is initially  $\tilde{w}_0$  as has been mentioned before. The law of conservation of energy then states that

$$\left(\frac{dr}{dt}\right)^2 + r^2 \left(\frac{d\varphi}{dt}\right)^2 - \tilde{w}_0^2 = -\frac{2\epsilon_p}{\bar{m}} \quad (13.4)$$

where  $-\epsilon_p$  is the positive work of the attractive force. The second summand is determined from the law of areas,  $r^2(\partial\varphi/\partial t) = \text{constant}$ , the left hand side of which equation, the moment of area divided by the mass, is initially  $\tilde{w}_0 r_0$ . The former equation then becomes

$$\left(\frac{dr}{dt}\right)^2 + \frac{1}{r^2} r_0^2 \tilde{w}_0^2 - \tilde{w}_0^2 = -\frac{2\epsilon_p}{\bar{m}} \quad (13.5)$$

The point of closest approach,  $r_{\min}$ , is defined by the usual conditions for a minimum

$$\left(\frac{dr}{dt}\right)_{\min} = 0$$

and therefore

$$\frac{r_0^2}{r_{\min}^2} = 1 - \frac{2\epsilon_p}{\bar{m}\tilde{w}_0^2} \quad (13.6)$$

A collision will occur for all values of  $r_0$  for which  $r_{\min} \leq d$ , i.e., when

$$r_0^2 \leq d^2 \left(1 - \frac{2\epsilon_p}{\bar{m}\tilde{w}_0^2}\right) \quad (13.7)$$

Upon suitable averaging over  $1/\tilde{w}_0^2$ , whereby it is to be noted that  $\tilde{w}_0^2$  is, on the average

The values of  $C$  calculated from the experimental data vary from 50 to 1,000, and increase with increasing attractive forces. They are proportional to the work obtained when two molecules are brought close together. The factor of proportionality, however, still depends upon the special form of the law of force between the molecules (Section 21). Since the Sutherland constant  $C$  is related to the forces between the molecules and to their diameters, it is also closely connected with the van der Waals constants  $a$  and  $b$ , the latent heat of evaporation, etc. In general these quantities are large for high boiling liquids and vice versa. Keyes<sup>4</sup> has shown that  $C$  is directly proportional to the Lorenz-Lorentz molecular polarization. Rankine<sup>5</sup> found empirically that  $C = T_c/1.12$ , where  $T_c$  is the critical temperature, but Vogel<sup>6</sup> changed this to  $C = 1.47T_b$ , where  $T_b$  is the boiling point. A comparison with experiments is given by Arnold.<sup>7</sup>

Discussion of some older papers can be found in the 2d ed. of this treatise, Vol. I, p. 129. For later developments, see Section 21.

### THE THEORY OF THE GASEOUS STATE

There will now be given a rigorous proof of Maxwell's distribution law<sup>8</sup> and an outline of the exact methods used to attack the problems of gases not at equilibrium.

(14) **The Boltzmann Equation:** The gas under consideration will be assumed to be composed of spherical molecules. At any instant throughout the gas some distribution of the density of the molecules and their velocities will exist. The spatial distribution of the molecules may be represented in the usual three-dimensional space described by the rectangular coordinates  $x, y, z$ , in which there is a state point for each molecule. Similarly, the distribution of the molecular velocities may be represented in the "velocity space" described by the rectangular coordinates  $\xi, \eta, \zeta$  (Section 2). The general distribution function  $f$ , which is to be evaluated, will therefore give the densities of the state points in these two systems of coordinates in terms of the coordinates.

proportional to  $T$  (cf. Equation [13.2]), the condition of collision becomes

$$r_0^2 \leq d^2 \left( 1 + \frac{C}{T} \right) \quad (13.8)$$

instead of

$$r_0^2 \leq d^2 \quad (13.9)$$

the factor signifying a *greater effective molecular diameter* at low temperatures.

<sup>4</sup> F. G. Keyes, *Z. Physik. Chem.*, **130**, 709 (1927).

<sup>5</sup> *Proc. Roy. Soc., A*, **84**, 190 (1910).

<sup>6</sup> *Ann. Physik*, **43**, 1235 (1914).

<sup>7</sup> *J. Chem. Phys.*, **1**, 170 (1933).

<sup>8</sup> Clerk Maxwell, *Phil. Mag.*, **35**, 185 (1868); *Phil. Trans. Roy. Soc.*, **170**, 231 (1880); L. Boltzmann, *Wien. Ber.*, **58**, 517 (1868); **66**, 275 (1872); **96**, 891 (1887); H. A. Lorentz, *ibid.*, **95**, 115 (1887). In Section 7 we assumed the thermodynamical result of equal kinetic energy throughout. No such assumption will be made now; accordingly this result will be a kinetic proof of the assumption.

It must be emphasized that the prevailing distribution is altered or maintained by the *irregularity* of the molecular collisions. Suppose, for example, that, at a given instant, some particular molecule is stationary. This molecule would remain motionless indefinitely if it experienced only balanced collisions, that is to say, if the effect of each molecule hitting the stationary one were exactly compensated by the impact of another molecule hitting the stationary one at the same time at a point diametrically opposite the point of collision of the first and with a velocity equal and opposite to that of the first. Such a regular sequence, however, can only occur infrequently; the stationary molecule is set in motion as a result of the irregularity of the collisions.

Consider now a gas in which the velocity and space distributions are arbitrary. In general the gas will not be at equilibrium. It will be necessary to investigate in detail how this arbitrary distribution will change in the course of time as a result of collisions between molecules, motions of the molecules and external forces.

In order to find the formula for the space and velocity distributions of the molecules it will be convenient to select a particular group of molecules and investigate the change in the number of molecules in this group. The conditions which must be fulfilled by a molecule in order that it be a member of this selected group will be first, its spatial coordinates must be in the intervals  $x$  to  $x + \Delta x$ ,  $y$  to  $y + \Delta y$  and  $z$  to  $z + \Delta z$ , and second, its components of velocity must be within the limits  $\xi$  and  $\xi + \Delta\xi$ ,  $\eta$  and  $\eta + \Delta\eta$ ,  $\zeta$  and  $\zeta + \Delta\zeta$ . In other words, the molecule's statepoint in the  $x, y, z$  space must be within the element of volume  $\Delta V$  at  $x, y, z$  and in the velocity space must be within an element of volume  $\Delta\omega = \Delta\xi\Delta\eta\Delta\zeta$  at the point  $\xi, \eta, \zeta$ . A molecule fulfilling these two conditions will be said to belong to group A.

The number of molecules in Group A will be proportional to  $\Delta V$  and  $\Delta\omega$  provided these are chosen neither too large nor too small (cf. Section 2). It will furthermore be proportional to the distribution function  $f$ , which, in the general case, will be a function of  $x, y, z$  and  $\xi, \eta, \zeta$ . Therefore

$$\Delta N = Nf(x, y, z, \xi, \eta, \zeta)\Delta V\Delta\omega \quad (14.1)$$

where  $\Delta N$  is the number of molecules in Group A,  $N$  the total number of molecules present and  $f$  the distribution function to be evaluated.

Now  $\Delta N$  can change in the course of time by means of three different processes. In the first place, each time a molecule of Group A experiences a collision its velocity is changed by a finite amount and it is therefore removed from the group. It will therefore be necessary to calculate in detail the number of collisions experienced by the molecules of Group A. To do this a new class of molecules (Group B) will be taken under consideration. To belong to this group a molecule's statepoints must lie within the elements  $\Delta V$ , and  $\Delta\omega_1$ , situated at the points  $x, y, z$ , and  $\xi_1, \eta_1, \zeta_1$ . The number of molecules in Group B will be

$$\Delta N_1 = Nf(x, y, z, \xi_1, \eta_1, \zeta_1)\Delta V\Delta\omega_1 \quad (14.2)$$

For abbreviation the arguments of the distribution function will be omitted, the appropriate subscripts being appended to the symbol  $f$ . Thus Equation (14.2) will be written

$$\Delta N_1 = N f_1 \Delta V \Delta \omega_1 \quad (14.3)$$

By a method of reasoning entirely similar to that developed in Section (11), it is found that the number of collisions per second between a single molecule of Group A and all the molecules of Group B is

$$\frac{\Delta N_1}{\Delta V} Z \quad (14.4)$$

where  $Z$  is a quantity depending on the nature of the molecule and the type of collision. If the molecules are perfectly elastic, hard spheres

$$dZ = d^2 |\bar{w}| \cos \vartheta \sin \vartheta d\vartheta d\varphi \quad (14.5)$$

where  $d$  is the molecular diameter,  $|\bar{w}|$  is the magnitude of the relative velocity,  $\vartheta$  the angle between the direction of the relative velocity and the line of centers at the instant of collision, and  $\varphi$  an angle determining the orientation of the plane containing the line of centers and the direction of the relative velocity. The quantity  $dZ$  is the contribution made to  $Z$  by those collisions for which the angles  $\vartheta$ ,  $\varphi$  lie within prescribed limits. Substituting from Equations (14.3) and (14.5), the expression (14.4) becomes  $N f_1 \Delta \omega_1 Z$ . In order to determine the total number of collisions experienced by a molecule of Group A,  $\xi_1$ ,  $\eta_1$ ,  $\zeta_1$  must be integrated over all values. Multiplying by the number of molecules in Group A ( $\Delta N$ , Equation [14.1]) the total number of collisions experienced by the molecules of Group A is found to be

$$N f \Delta V \Delta \omega N \int_{\omega_1} Z f_1 d\omega_1 = N^2 \Delta V \Delta \omega \int_{\omega_1} Z f f_1 d\omega_1 \quad (14.6)$$

This is therefore the number of molecules leaving Group A per unit time as a result of collisions. On the other hand, some molecules formerly not belonging to Group A will be thrown into it by collisions. It will now be necessary to calculate the number of these molecules entering Group A as a result of their collisions.

The velocity of a molecule of Group A after collision will be denoted by  $\xi^*$ ,  $\eta^*$ ,  $\zeta^*$ , and that of a molecule of Group B after collision with the molecule of group A by  $\xi_1^*$ ,  $\eta_1^*$ ,  $\zeta_1^*$  (Groups A\* and B\*).  $\xi^* \cdots \zeta_1^*$  will depend on  $\xi \cdots \zeta_1$ , on  $\vartheta$  and  $\varphi$  and on the nature of the molecules.

Now the process of molecular collision is mechanically reversible, that is, if a collision between a molecule of Group A and one of Group B changes them to Groups A\* and B\* respectively, then a collision between molecules of Groups A\* and B\* will result in molecules of Groups A and B provided  $\vartheta$  and  $\varphi$  for the two collisions are properly related (see Fig. 21).

The number of collisions of a particular type between a particular Group A\* and a particular Group B\*, which results in molecules of Group A and

Group B after collision, is given by

$$N^2 f_1^* dZ^* \Delta V^* d\omega^* d\omega_1^* \quad (14.7)$$

as reasoning similar to that which led to (14.6) will prove. Here, e.g.,  $d\omega^*$  is the volume element in the velocity space filled by the state points of Group A\*. It can now be shown that

$$\Delta V^* = \Delta V, \quad \text{and} \quad dZ^* d\omega^* d\omega_1^* = dZ d\omega d\omega_1$$

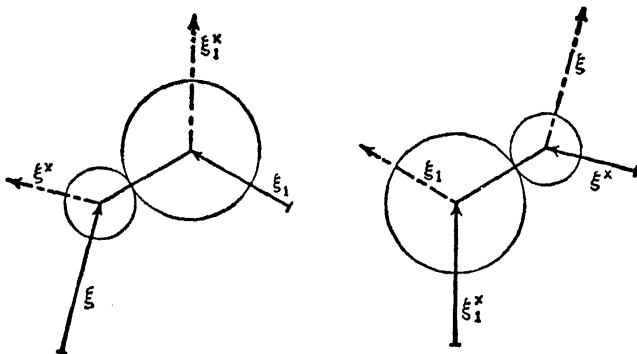


FIG. 21.

where  $d\omega$  is the volume element in the velocity space filled by the statepoints of molecules in Group A which result from the collision, and similarly for the other quantities.

The proof is as follows. The collision only changes the velocities, not the space filled by the molecules, therefore,  $\Delta V^* = \Delta V$  follows directly. Next, use the velocity of the center of gravity and the relative velocity instead of the individual velocities of the two molecules, as in Section 4. It is then found that

$$d\omega d\omega_1 = d\xi_c d\eta_c d\xi_c \tilde{w}^2 d\tilde{w} d\Omega$$

where  $d\Omega$  is the solid angle within which the group of relative velocities lies before collision. But neither the motion of the center of gravity, nor the speed  $\tilde{w}$  is at all affected by the collision, and from the geometry of the collisions, it is seen that

$$dZ^* d\Omega^* = dZ d\Omega$$

Therefore (14.7) can be changed into the form

$$N^2 f_1^* dZ \Delta V d\omega d\omega_1$$

where  $dZ$ ,  $\Delta V$ ,  $d\omega$ , and  $d\omega_1$  refer to the state after collision of the Groups A\* and B\*. Therefore the total number of molecules newly brought into Group A

through collision between any Group A\* and B\* is

$$N^2 \Delta V dw \iint f^* f_1^* dZ d\omega_1$$

and the net decrease in the number of molecules in Group A through collisions is

$$N^2 \Delta V \Delta \omega \iint (ff_1 - f^* f_1^*) dZ d\omega_1 \quad (14.8)$$

The second way in which the number of molecules of Group A can change is by motion of the molecules in and out of the *volume* element. The number

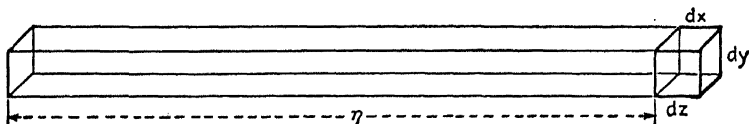


FIG. 22.

of molecules crossing the boundary perpendicular to the  $x$ -axis at the point  $x$  from left to right will be (Fig. 22, and Section 3)

$$\xi \left( \frac{\Delta N}{\Delta V} \right)_x \Delta y \Delta z = N \xi f_x \Delta \omega \Delta y \Delta z \quad (14.9)$$

This is the number of molecules entering Group A per second through this face of the cubical element of volume. The flow of molecules from left to right through the opposite face of the element equals

$$\xi \left( \frac{\Delta N}{\Delta V} \right)_{x+\Delta x} \Delta y \Delta z = N \xi f_{x+\Delta x} \Delta \omega \Delta y \Delta z \quad (14.10)$$

If the density is not everywhere the same  $f_x$  is not equal to  $f_{x+\Delta x}$  but

$$f_{x+\Delta x} = f_x + \frac{\partial f}{\partial x} \Delta x \quad (14.11)$$

Therefore, the net loss to Group A by flow through these two boundaries of the cube is

$$N \xi \left( f_x + \frac{\partial f}{\partial x} \Delta x - f_x \right) \Delta \omega \Delta y \Delta z = N \xi \frac{\partial f}{\partial x} \Delta \omega \Delta V \quad (14.12)$$

Taking account of the flow through the other two pairs of faces of the cube, the total net loss to Group A resulting from motion of the molecules between collisions is found to be

$$N \left( \xi \frac{\partial f}{\partial x} + \eta \frac{\partial f}{\partial y} + \zeta \frac{\partial f}{\partial z} \right) \Delta \omega \Delta V \quad (14.13)$$



The third way in which the number of molecules in Group A can be changed is by the action of external forces which change the molecular velocities during the intervals between collisions and therefore cause the statepoints in the velocity space to move in or out of  $\Delta\omega$  in a continuous manner. (At collisions they *jump* to another place in the velocity space.) Consider a field of force, the intensity of which at any point may be represented by the components of force  $F_x$ ,  $F_y$ ,  $F_z$  acting at that point. Then the equations representing the motion of the molecules between collisions are

$$m \frac{d\xi}{dt} = F_x; \quad m \frac{d\eta}{dt} = F_y; \quad m \frac{d\zeta}{dt} = F_z; \quad (14.14)$$

where  $m$  is the mass of the molecule and  $t$  the time. The present calculation is exactly similar to the preceding except that instead of calculating the flux of molecules moving with the velocity  $\xi$ ,  $\eta$ ,  $\zeta$  through the boundaries of the element  $\Delta V$  the problem now requires the calculation of the flux of statepoints in the velocity-space moving with the velocity  $d\xi/dt$ ,  $d\eta/dt$ ,  $d\zeta/dt$  through the boundaries of the element  $\Delta\omega$ . The net loss to Group A as a result of the external forces is therefore

$$N \left( \frac{d\xi}{dt} \cdot \frac{\partial f}{\partial \xi} + \frac{d\eta}{dt} \cdot \frac{\partial f}{\partial \eta} + \frac{d\zeta}{dt} \cdot \frac{\partial f}{\partial \zeta} \right) \Delta\omega \Delta V \quad (14.15)$$

which, by Equations (14.14), equals

$$N \left( \frac{F_x}{m} \cdot \frac{\partial f}{\partial \xi} + \frac{F_y}{m} \cdot \frac{\partial f}{\partial \eta} + \frac{F_z}{m} \cdot \frac{\partial f}{\partial \zeta} \right) \Delta\omega \Delta V \quad (14.16)$$

Equations (14.8), (14.13) and (14.16) give the decreases in the number of molecules in Group A due to collisions, motion of the molecules and external forces. The sum of these three quantities must equal the total decrease in the number of molecules in Group A which is

$$- N \frac{\partial f}{\partial t} \Delta\omega \Delta V$$

Therefore, after dividing through by  $N\Delta\omega\Delta V$ , there is obtained the fundamental equation of the theory of gases <sup>1</sup>

$$\begin{aligned} \frac{\partial f}{\partial t} + \frac{F_x}{m} \frac{\partial f}{\partial \xi} + \frac{F_y}{m} \frac{\partial f}{\partial \eta} + \frac{F_z}{m} \frac{\partial f}{\partial \zeta} + \xi \frac{\partial f}{\partial x} + \eta \frac{\partial f}{\partial y} + \zeta \frac{\partial f}{\partial z} \\ = - N \int_{\omega_1} Z(f_1 - f^* f_1^*) d\omega_1 \quad (14.17) \end{aligned}$$

<sup>1</sup> L. Boltzmann, *Wien. Ber.*, **66**, 213 (1872); **72**, 427 (1875). For a treatment involving the theory of relativity, see F. Jüttner, *Ann. Physik*, **34**, 856 (1911); E. Kretschmann, *Physik. Z.*, **21**, 484 (1920); **25**, 162 (1924). The equation in case the Pauli exclusion principle is applicable is discussed by L. Nordheim, *Proc. Roy. Soc.*, **A119**, 689 (1928); G. E. Uhlenbeck and E. A. Uehling, *Phys. Rev.*, **39**, 1014 (1932); **43**, 552 (1933).

In the case of a mixture of two gases there must be added another term to take account of the collisions between molecules of the two different gases. This term is

$$-d_{12}^2 N' \int (ff_1' - f^* f_1'^*) d\xi' d\eta' d\zeta' \int |\tilde{w}_{12}| \cos \vartheta \sin \vartheta d\vartheta d\varphi \quad (14.18)$$

where the primed symbols denote the corresponding quantities for the second component of the mixture. An entirely analogous expression holds for the other constituent itself.

Furthermore, if it is assumed that the molecules no longer are elastic spheres, but act upon each other according to some law of force, the only change in the fundamental equation is to replace the constant cross section  $\pi d^2$  of the molecules with one dependent on the velocity and to change the formal relation between the velocities before and after collision.

**(15) Gases in Equilibrium:** In the simplest case of equilibrium in which there are no external forces and where the density is constant throughout the space under discussion, the left hand side of Equation (14.17) must be zero since, in this particular case,  $f$  is not a function of  $x, y, z$ . A sufficient condition that the integral on the right shall vanish is that at every point of the velocity space

$$ff_1 = f^* f_1^* \quad (15.1)$$

Since, furthermore, in this case there is no favored direction of velocity,  $f$  can only depend on the magnitude of the velocity  $w = \sqrt{\xi^2 + \eta^2 + \zeta^2}$  and not upon the individual components  $\xi, \eta, \zeta$ . Therefore

$$f(w)f(w_1) = f(w^*)f(w_1^*) \quad (15.2)$$

Now  $w$  and  $w_1$  are entirely arbitrary and  $w^*$  may be arbitrarily varied to a certain extent by changing the angle  $\vartheta$ ;  $w_1^*$  is then determined by the law of conservation of energy,

$$w_1^{*2} = w^2 + w_1^2 - w^{*2} \quad (15.3)$$

With this value of  $w_1^*$  Equation (15.2) can only be satisfied for arbitrary values of  $w, w_1$  and  $w^*$  if <sup>1</sup>

$$f = Ae^{-\beta m w^2} \quad (15.9)$$

<sup>1</sup> Define a function

$$\varphi(w^2) = \ln f(w) \quad (15.4)$$

Then

$$\varphi(w^2) + \varphi(w_1^2) = \varphi(w^{*2}) + \varphi(w^2 + w_1^2 - w^{*2}) \quad (15.5)$$

Upon differentiating this with respect to  $w$ , keeping the other independent variables  $w_1$  and  $w^*$  constant, this becomes

$$2w\dot{\varphi}(w^2) = 2w\dot{\varphi}(w^2 + w_1^2 - w^{*2}) \quad (15.6)$$

where  $\dot{\varphi}(x) = d\varphi/dx$ . Since the left hand side of this does not contain  $w_1$  and  $w^*$ , the right hand side must also be independent of these quantities. Therefore

$$\dot{\varphi}(w^2) = -B \quad (15.7)$$

and

$$\varphi(w^2) = -Bw^2 + \text{const} \quad (15.8)$$

which is Maxwell's distribution law for the state of equilibrium. For a mixture of several gases, the analogous formula is

$$f(w)f'(w_1') = f(w^*)f'(w_1'^*) \quad \text{and} \quad m'w_1'^{*/2} = mw^2 + m'w_1'^{1/2} - mw^{*2} \quad (15.10)$$

whence

$$f' = A'e^{-\beta m'w'^2} \quad (15.11)$$

The magnitude  $\beta$  is therefore identical for all the components of the gaseous mixture. Further,  $1/\beta$  is seen to be  $4/3$  times the mean kinetic energy, and the latter is therefore the same for all the components of the mixture. Considerations such as those of Section 4 show the equality of this quantity for any two gases placed in thermal contact and therefore its significance as a measure of the temperature.

If the gas is situated in a field of force such that

$$F_x = -\frac{\partial \epsilon}{\partial x}; \quad F_y = -\frac{\partial \epsilon}{\partial y}; \quad F_z = -\frac{\partial \epsilon}{\partial z}; \quad (15.12)$$

the Maxwell-Boltzmann law follows at once from Equation (14.17).

It can also be seen that if the whole gas is streaming uniformly with the constant velocity  $W$ , which has the components  $W_x, W_y, W_z$ , the Maxwell distribution is correct for an observer moving with the gas; then

$$Nf = \frac{N}{V} \left( \frac{m}{2\pi kT} \right)^{3/2} e^{-\frac{m}{2kT} \{ (\xi - W_x)^2 + (\eta - W_y)^2 + (\zeta - W_z)^2 \}} \quad (15.13)$$

which is also a solution of (15.1).

(16) **Gases Not in Equilibrium:** In case of non-equilibrium, the entire Equation (14.17) must be solved. This equation, however, contains the unknown  $f$  quadratically, which makes the difficulties prohibitive. Therefore, the treatment is restricted to those cases, which seem to cover normal viscosity, heat conduction, diffusion, and the like, where the deviation from the Maxwell distribution is small. In the calculation, higher powers of this deviation are usually neglected.<sup>1</sup>

The procedure is as follows. One is still free to make a decision about the particular kind of Maxwell distribution from which to start in calculating the deviation. The density of the gas is then defined as  $\rho$  (i.e., for uniform density  $mN/V$ ), which, however, may vary from place to place, so that

$$\rho = Nm \int f d\omega \quad (16.1)$$

Furthermore,  $W_x, \dots$  are the components of the local bulk velocity of the gas,

<sup>1</sup> Higher terms are considered by J. E. Lennard-Jones, *Phil. Trans. Roy. Soc.*, **223**, 1 (1923); M. Brillouin, *Ann. chim. phys.*, **20**, 440 (1900); K. F. Herzfeld, *Ann. Physik*, **23**, 456, 476 (1935). D. Burnett, *Proc. London Math. Soc.*, **39**, 385 (1935).

which may vary in time and space. Therefore,

$$W_x = \int \xi f d\omega; \quad W_y = \int \eta f d\omega \quad (16.2)$$

Finally, the temperature is defined by the average local kinetic energy

$$\frac{3}{2}kT = \int \frac{1}{2}m[(\xi - W_x)^2 + (\eta - W_y)^2 + (\zeta - W_z)^2]f d\omega \quad (16.3)$$

The Maxwell distribution function  $F$  is then defined by

$$F = \frac{\rho}{m} \left( \frac{m}{2\pi kT} \right)^{3/2} e^{-\frac{m}{2kT}[(\xi - W_x)^2 + (\eta - W_y)^2 + (\zeta - W_z)^2]} \quad (16.4)$$

and the distribution function by

$$f = F(1 - \Lambda\Phi) \quad (16.5)$$

Here,  $\Lambda$  is the mean free path (or a length proportional to it), and  $\Phi$  is the unknown function. A considerable knowledge of  $\Phi$  can be gained from very general considerations. If the density, flow velocity, and temperature were uniform, the distribution would be Maxwellian. Therefore, the deviation from the Maxwell distribution should depend on the variation of these quantities from place to place. In first approximation,  $\Phi$  can be made proportional to the differential quotient of the temperature, bulk velocity, etc. with respect to the coordinates.

As an example, let us consider the temperature gradient. We expect that  $\Phi$  will contain a term  $\Phi_1'(\xi, \eta, \zeta, T)\partial T/\partial X$ . Now  $\Lambda\Phi$  must be dimensionless, being added to unity.  $\partial T/\partial X$  has the dimensions Temperature/Length; hence,  $\Phi_1'$  must have the dimensions (Temperature)<sup>-1</sup>. We find, therefore, that the factor preceding  $\partial T/\partial X$  is  $1/T$  times a dimensionless function.

We then use the fact that the general form of  $f$  must be independent of the particular coordinate system used. Now let us assume that we change our coordinate system so that we count  $+X$  to the left and  $-X$  to the right. Then, in a given case  $\partial T/\partial X$  changes sign, while  $\Phi$  must remain numerically unchanged because it is a scalar quantity, not having direction; consequently, the sign change in  $\partial T/\partial X$  must be compensated by a sign change in  $\Phi_1'$ ; but the only quantity in  $\Phi_1'$  that changes sign under this procedure is  $\xi$  which, therefore, must appear as a factor, or more specifically as a factor in the form  $\xi\sqrt{m/2kT}$  so that it may be dimensionless. Furthermore, if the gradient is only in the  $x$ -direction, nothing is changed by exchanging  $y$  and  $-y$ , so that  $\eta$  can only appear as  $\eta^2$  (and similarly  $\zeta$  as  $\zeta^2$ ). Finally, if we rotate the system of coordinates around the  $x$ -axis, nothing changes, so that  $\eta$  and  $\zeta$  can only appear in the combination  $\eta^2 + \zeta^2$  which has a value independent of the particular rotation of the system, since it is the square of the projection of the velocity on the  $yz$ -plane. We end up by having the part in  $\Phi$  that comes

from  $\partial T/\partial X$  of the form

$$(1/T)\xi\sqrt{m/2kT}\Phi_1''[(m\xi^2/2kT); m(\eta^2 + \zeta^2)/2kT]\partial T/\partial X \quad (16.6)$$

the factor  $m/2kT$  being included to make  $m\xi^2/2kT$  dimensionless. If the temperature gradient has arbitrary direction, we get as contribution to  $\Phi$

$$(1/T)\sqrt{m/kT}\{\xi(\partial T/\partial X)\Phi_1''[(m\xi^2/2kT); (m/2kT)(\eta^2 + \zeta^2)] \\ + \eta(\partial T/\partial Y)\Phi_1''[(m\eta^2/2kT); (m/2kT)(\xi^2 + \zeta^2)] \\ + \zeta(\partial T/\partial Z)\Phi_1''[(m\zeta^2/2kT); (m/2kT)(\xi^2 + \eta^2)] \quad (16.7)$$

The quantities enclosed in [ ] are arguments of the function  $\Phi''$ .

If finally we wish to obtain formally the same expression if the coordinate system is rotated arbitrarily, it turns out that  $\Phi_1''$  contains only  $\xi^2 + \eta^2 + \zeta^2 = w^2$ , so that the contribution to  $\Delta\Phi$  from the temperature gradient is <sup>2</sup>

$$\Delta \frac{1}{T} \sqrt{\frac{m}{2kT}} \Phi_1 \frac{mw^2}{2kT} \left( \xi \frac{\partial T}{\partial X} + \eta \frac{\partial T}{\partial Y} + \zeta \frac{\partial T}{\partial Z} \right) \quad (16.8)$$

Proceeding in the same manner with the velocity gradient it is found that

$$\Delta\Phi = \Delta\Phi_1\{\xi(\partial T/\partial X) + \eta(\partial T/\partial Y) + \zeta(\partial T/\partial Z)\}(1/T)\sqrt{m/2kT} \\ + \Delta P \left\{ \xi^2 \left( 2 \frac{\partial W_x}{\partial x} - \frac{\partial W_y}{\partial y} - \frac{\partial W_z}{\partial z} \right) \right. \\ + \eta^2 \left( 2 \frac{\partial W_y}{\partial y} - \frac{\partial W_x}{\partial x} - \frac{\partial W_z}{\partial z} \right) + \dots \\ \left. + 3\xi\eta \left( \frac{\partial W_x}{\partial y} + \frac{\partial W_y}{\partial x} \right) + \dots \right\} \left( \frac{m}{2kT} \right)^{3/2} \quad (16.9)$$

Here both  $\Phi_1$  and  $P$  are functions of  $mw^2/2kT$  only. They do not depend on the particular state of the gas, but on the details of the collisions and through them on the law of force between the molecules. It is the calculation of these functions which necessitates the use of the Boltzmann equation.

Considerable work has been devoted to this calculation. Boltzmann<sup>3</sup> first introduced the method described above; it was then used extensively by Lorentz.<sup>4</sup> The mathematical principles underlying the solvability of an equation like (14.17) were brought into systematical form by Hilbert.<sup>5</sup> Enskog<sup>6</sup> made the calculations for the following types of molecules: elastic spheres, points repelling each other with forces proportional to  $Kr^{-n}$ , elastic spheres with attraction.

<sup>2</sup> In mathematical language that is the only scalar that one can build from the first power of the temperature gradient vector.

<sup>3</sup> *Loc. cit.*, also *Ges. Abh.* II, p. 388 ff.; III, p. 3; *Gasttheorie*, I, p. 184.

<sup>4</sup> *Arch. neerl.*, 16, 1 (1881).

<sup>5</sup> *Vorlesungen über Integralgleichungen* (Leipzig: 1912).

<sup>6</sup> *Diss. Upsala* (1917); *Physik. Z.*, 12, 56, 533 (1911); *Ark. för Mat. Astr. och Fysik*, 16, No. 16 (1921).

Great progress was made in recent years by Burnett,<sup>7</sup> who discovered a method analogous to "harmonic analysis" for the solution of (16.9). He introduced a type of function not used hitherto, into which  $\Phi_1$  and  $P$  are developed.

A somewhat different method of solution had been used by Maxwell<sup>8</sup> and followed by Chapman.<sup>9</sup> It consists in applying the considerations of the preceding section not to the distribution function itself, but to any quantities which are definite for every molecule. Applications to certain simple cases will be explained in the next section. Chapman used for example  $\xi^2 w^{2n}$  and gets equations for the change of the *average value* of this expression with time and space. From such equations for a large number of these quantities, conclusions can be drawn as to the distribution function. In this manner Chapman developed  $\Phi_1$  and  $P$  into power series of  $mw^2/2kT$  and determined the coefficients for the same types of molecules as did Enskog.

Maxwell had limited his developments of  $\Phi_1$  and  $P$  to the terms independent of and linear in  $mw^2/2kT$ . Only if the forces between molecules are proportional to  $r^{-4}$  was it possible to get exact results, but it is known today that such forces do not exist between neutral molecules.

(17) **The Equations of Motion of the Gas:** From the standpoint of the kinetic theory, it is simple to express the macroscopic quantities which are needed to describe the behavior of the gas in bulk. They are the density, the stresses and the energy flow. Only if the gas is at rest do we have a hydrostatic pressure, equal in all directions. In a moving gas, the stresses are more complicated and form a "tensor," i.e., a quantity with components that have to be characterized by two indices. If a surface, e.g., normal to the  $z$ -axis is considered, the stresses (forces on a unit area) exerted on it can be divided into two groups: the stress normal to it, i.e., parallel to  $Z$ , which is called  $p_{zz}$ , and a shearing stress parallel to the surface which can be divided into two components,  $p_{zx}$ , exerted in the direction of the  $x$ -axis, and  $p_{yz}$ , exerted in the direction of the  $y$ -axis (both are in the plane considered). For hydrostatic pressure, all the shearing stresses are zero and all the normal stresses equal.

According to kinetic theory all mechanical effects on a plane are due to the momentum transported by the molecules coming toward and from the plane. A molecule coming toward the plane normal to the  $z$ -axis has a transport velocity  $\zeta$  and transports momentum with the components  $m\xi$ ,  $m\eta$ ,  $m\zeta$ . Therefore the stresses are given by

$$\begin{aligned} p_{zz} &= N \iiint m\zeta\zeta f d\xi d\eta d\zeta \\ p_{yz} &= N \iiint m\eta\zeta f d\xi d\eta d\zeta, \text{ etc.} \end{aligned} \quad (17.1)$$

<sup>7</sup> *Proc. London Math. Soc.*, **39**, 385 (1935); **40**, 382 (1936).

<sup>8</sup> *Phil. Trans. Roy. Soc.*, **157**, 49 (1867); *Phil. Mag.*, **35**, 129, 185 (1868).

<sup>9</sup> *Phil. Trans. Roy. Soc.*, **211**, 433 (1912); **216**, 279 (1916); **217**, 115 (1917); *Proc. Roy. Soc.*, **A**, **93**, 1 (1912).

Similarly, energy is transported by the movement of the molecules. If the gas is monatomic, so that all the energy is kinetic, a molecule transports in the  $x$ -direction  $\xi m(\xi^2 + \eta^2 + \zeta^2)/2$ . The heat flow is then a vector, whose  $x$ -component is

$$N \int \xi(\frac{1}{2}m)(\xi^2 + \eta^2 + \zeta^2) f d\xi d\eta d\zeta \quad (17.2)$$

If there is also a bulk motion of the gas present, this expression includes both convection and conduction.

To obtain the equations of motion, the method of Maxwell is used, as was done by Lorentz and Hilbert, and the changes in the number of molecules, the average momentum, and the average energy are considered. Each one of these quantities is preserved for a pair of molecules in a collision and therefore none of these is changed by the collisions as a whole. Writing the equations for the total change of these quantities in the manner of (14.17), the right side is zero, and we obtain the hydrodynamical equations in the following manner:

Change of total number of molecules in the unit volume:

Equation of continuity.

Change of the total linear momentum (three components):

Equations of motion (one for each coordinate).

Change of total energy:

Equation of heat conduction.

These equations are usually written up to the approximation outlined by (16.5).<sup>1</sup> If Maxwell's distribution  $F$  is used as a first approximation, there is obtained the equation for a non-viscous liquid without heat conduction (that is, at uniform temperature) and with the equation of state  $pV = RT$ .

When the different macroscopic quantities are expressed by molecular quantities, it is usually necessary to calculate the amount of transfer of certain molecular quantities (linear momentum, energy, etc.) by collision. In this calculation certain integrals  $\Omega$  occur, which have been defined by Chapman and Cowling.<sup>2</sup>

<sup>1</sup> These equations are ( $\rho$  = density)

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x}(\rho W_x) + \frac{\partial}{\partial y}(\rho W_y) + \frac{\partial}{\partial z}(\rho W_z) \quad (17.3)$$

$$\rho \left( \frac{\partial W_x}{\partial t} + W_x \frac{\partial W_x}{\partial x} + W_y \frac{\partial W_x}{\partial y} + W_z \frac{\partial W_x}{\partial z} \right) \\ = - \frac{\partial p}{\partial x} + \frac{\eta}{3} \left\{ 4 \frac{\partial^2 W_x}{\partial x^2} + \frac{\partial}{\partial y} \left( 3 \frac{\partial W_x}{\partial y} + \frac{\partial W_y}{\partial x} \right) + \frac{\partial}{\partial z} \left( 3 \frac{\partial W_x}{\partial z} + \frac{\partial W_z}{\partial x} \right) \right\} \quad (17.4)$$

and two others (for  $y$  and  $z$ )

$$RT_c \left( \frac{\partial W_x}{\partial x} + \frac{\partial W_y}{\partial y} + \frac{\partial W_z}{\partial z} \right) - \lambda \left( \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right) \times \frac{3}{2} R_c \frac{DT}{Dt} \quad (17.5)$$

<sup>2</sup> We follow the notation in S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-uniform Gases* (Cambridge University Press, 1939).

Assume a molecule 1 moving toward a molecule 2 with a relative velocity  $\tilde{w}$ . Assume that the shortest distance at which the two molecules would pass each other, if they both were points located at the respective centers and had no interaction, is  $\sigma$ . Then the number of such "collisions" per second in unit volume is  $N_1 N_2 \tilde{w} 2\pi\sigma d\sigma$ . Call  $\psi$  the angle which the velocity of molecule 1 makes after the encounter with the velocity before the encounter:  $\psi$  depends on  $\sigma$  and  $\tilde{w}$ . For hard molecules, if  $\vartheta$  is the angle which the line of centers at collision makes with the original velocity

$$\sigma = \frac{1}{2}(d_1 + d_2) \sin \vartheta \quad \text{and} \quad \psi = \pi - 2\vartheta \quad (17.6)$$

with  $\psi$  independent of  $\tilde{w}$ .

Chapman and Cowling<sup>3</sup> now define<sup>4</sup>

$$\Omega_{12}^{(l)}(r) = \frac{1}{2}\pi^{-\frac{1}{2}} \int_0^\infty e^{-\frac{mw^2}{2kT}} \left(\frac{mw^2}{2kT}\right)^{r+1} \frac{m}{2kT} dw \int_0^\infty (1 - \cos^l \psi) w 2\pi\sigma d\sigma, \quad (17.7)$$

where  $r$  and  $l$  are any two integers; the subscript refers to the interaction of two different kind of molecules, otherwise the subscript is 1 or 2.  $\Omega^{(1)}(1)$  appears in the first approximation for the coefficient of viscosity and that of heat conductions,  $\Omega^{(2)}(2)$  in the diffusion constant  $D$ .

For hard elastic molecules<sup>5</sup>

$$\Omega_{12}^{(l)}(r) = \frac{\pi^{\frac{1}{2}}}{8} d_{12}^2 \left(\frac{2kT}{m}\right)^{\frac{1}{2}} (r+1)! \left[2 - \frac{1}{(l+1)} (1 + (-1)^l)\right] \quad (17.8)$$

$$d_{12} = \frac{1}{2}(d_1 + d_2)$$

where  $(r+1)!$  represents the product of all positive integers up to and including  $r+1$ .

Hirschfelder<sup>6</sup> and his coworkers have assumed the following interaction energy between two molecules the centers of which are at distance  $r$

$$4\epsilon \left[ -\left(\frac{r_0}{r}\right)^6 + \left(\frac{r_0}{r}\right)^{12} \right] \quad (17.9)$$

Here  $r_0$  is the distance of nearest approach for head-on collisions of molecules starting with zero velocity from infinity.  $2^{\frac{1}{2}}r_0$  is the equilibrium distance and  $\epsilon$  the heat of dissociation of a pair.

Defining the function  $W$  by

$$\Omega_{(n)}^{(l)} = r_0^2 \left(\frac{2\pi kT}{m}\right)^{\frac{1}{2}} W^l \left(n, \frac{\epsilon}{kT}\right)$$

<sup>3</sup> *Op. cit.*, p. 157.

<sup>4</sup> Enskog introduces integrals  $\Omega^l(n)$  where  $n$  corresponds to Chapman's  $r$ ; Enskog's integrals contain the Legendre function of order  $l$ , instead of the cosine to the power  $l$ .

<sup>5</sup> Chapman and Cowling, *op. cit.*, p. 168.

<sup>6</sup> J. O. Hirschfelder, R. B. Bird and E. L. Spotz, *J. Chem. Phys.* 16, 968 (1948).



( $n$  taking the place of Chapman and Cowling's  $r$ ) they have given tables of  $W^1(1)$  to  $W^1(3)$ ,  $W^2(2)$  to  $W^2(6)$  and  $W^4(4)$ .

(18) **H-theorem:** The considerations which permit the calculation by means of Equation (14.17) of the change of some quantity in the element of volume due to collisions between the molecules, led Boltzmann<sup>1</sup> to a conclusion, which is of great importance to the theory of gases, in the course of an investigation of the change in the quantity  $\ln f$  summed over all the molecules. He defined a function  $H$  by the equation

$$H = N_0 \int \ln f \cdot f d\xi d\eta d\zeta dV \quad (18.1)$$

$H$  is calculated by introducing the coordinates and velocities of each molecule into  $\ln f$  and summing over all the molecules in the volume, that is, integrating over  $N_0 f d\xi d\eta d\zeta dV$ . If Equation (14.17) is multiplied through by  $\ln f N_0 d\xi d\eta d\zeta dV$  and integrated there is obtained upon the left  $dH/dt$ , the total change in the quantity  $H$  in the volume under consideration<sup>2</sup>

$$\frac{dH}{dt} = -N_0^2 \iint \ln f (ff_1 - f^*f_1^*) d\xi d\eta d\zeta d\xi_1 d\eta_1 d\zeta_1 dVZ \quad (18.2)$$

Since the integral of  $\ln f$  over *all* the molecules is the same regardless of the particular group which is used as a starting point,  $\ln f$  may be replaced in Equation (18.2) by  $(\ln f + \ln f_1)/2$ . The expression, however, is not yet sufficiently symmetrical.

Let us introduce besides the "direct collisions," the reverse collisions formerly designated by a star. There is then obtained the same value by writing

$$\frac{dH}{dt} = -N_0^2 \iint \frac{\ln f^* + \ln f_1^*}{2} (f^*f_1^* - ff_1) dV^* d\omega^* d\omega_1^* Z \quad (18.3)$$

Adding this to the former expression and dividing by 2 gives

$$\frac{dH}{dt} = -\frac{N_0^2}{4} \iint (\ln f_1 - \ln f^*f_1^*)(ff_1 - f^*f_1^*) d\xi d\eta d\zeta d\xi_1 d\eta_1 d\zeta_1 dVZ \quad (18.4)$$

The right hand side of this equation has always the same sign, since, whenever one of the parentheses changes sign, the other changes sign simultaneously.  $H$  is therefore a quantity which decreases in all possible processes involving deviations from the equilibrium value of  $f$ , and is therefore analogous to negative entropy.

<sup>1</sup> L. Boltzmann, *Wien. Ber.*, 66, 275 (1872); *Gastheorie*, I, p. 32, 124.

<sup>2</sup> More exactly

$$\frac{dH}{dt} = N_0 \int \left( \ln f \frac{df}{dt} + \frac{1}{f} \frac{df}{dt} \right) d\xi d\eta d\zeta dV$$

The last summand of this expression, however, vanishes upon integration, if the total number of molecules is constant.

As a matter of fact a direct calculation shows that

$$H = -(S/k) + \text{const} \quad (18.6)$$

Thus, a mechanical explanation is given of the experimental result that the entropy of a system always increases (Boltzmann's H-theorem).

(19) **Polyatomic Gases:** (a) *Classical Treatment for Diatomic Molecules:*<sup>1</sup> The greater part of the foregoing discussion has been concerned only with monatomic gases. Such a gas has only three degrees of freedom per molecule. Because of this fact the average kinetic energy of the molecule was found to be  $\frac{3}{2}kT$ . Since this is the only type of energy present in the gas,  $E = \frac{3}{2}RT$ . Correspondingly, the calculated value for the molar heat capacity is  $C_v = \frac{3}{2}R$ . As will be seen from the following table, this prediction is confirmed by experiment.

TABLE II  
MOLAR HEAT CAPACITIES OF MONATOMIC GASES

	$T^\circ \text{K}$	$C_v$	
He.....	291	3.008	Perfect gas interval <sup>1</sup>
	93	2.949	
	26	2.99	9.3 moles/liter <sup>2</sup>
	22	3.00	
	18	3.02	
A.....	288	3.07	Perfect gas interval <sup>3</sup>
	93	2.86	
Hg.....	$\sim 550$	2.97	Calculated from $C_p/C_v = 1.666$ <sup>4</sup>

<sup>1</sup> K. Scheel and W. Heuse, *Ann. Physik*, 40, 473 (1913).

<sup>2</sup> A. Eucken, *Verh. deut. phys. Ges.*, 18, 4 (1916).

<sup>3</sup> W. Heuse, *Ann. Physik*, 59, 86 (1919).

<sup>4</sup> A. Kundt and E. Warburg, *Pogg. Ann.*, 157, 353 (1876).

On the other hand, di- and poly-atomic gases have higher heat capacities.

Consider first a diatomic gas, the molecule of which (mass  $m$ ) contains two atoms of masses  $m_1$  and  $m_2$ , the distance between the two atoms being  $d$ . The center of gravity of the molecule is on the line joining the centers of the atoms and divides this line in such a manner that the distance from the center of gravity to atom I is

$$d_1 = d \frac{m_2}{m_1 + m_2} \quad (19.1)$$

and the distance from the center of gravity to atom II is

$$d_2 = d \frac{m_1}{m_2 + m_1} \quad (19.2)$$

<sup>1</sup> For quantum treatment, see this Treatise, 3rd ed., Vol. I, Chap. IV.

The molecule can now rotate about its center of gravity. In order to fix the orientation of the molecule imagine a straight line fixed in space which is to serve as the polar axis of a system of space polar coordinates having its origin at the center of gravity of the molecule in question. The position of the axis of the molecule is then determined by the geographical latitude,  $\frac{1}{2}\pi - \vartheta$ , and the geographical longitude,  $\varphi$ , of, for example, atom I. Atom I can therefore rotate on a sphere of radius  $d_1$ , element of surface  $d_1^2 \sin \vartheta d\vartheta d\varphi$  and total area  $4\pi d_1^2$ . The rotational kinetic energy of atom I can be resolved into two parts corresponding to the two components of velocity, one of which is along a parallel of latitude and the other is along a meridian of longitude. The first component of velocity is  $d_1 \sin \vartheta \dot{\varphi}$ ,  $d_1 \sin \vartheta$  being the radius of the particular parallel of latitude. The second component of velocity is  $d_1 \dot{\vartheta}$ . The rotational kinetic energy of atom I is therefore  $\frac{1}{2}m_1 d_1^2 (\dot{\vartheta}^2 + \sin^2 \vartheta \dot{\varphi}^2)$ , where the superposed dots signify derivatives with respect to the time (e.g.,  $\dot{\varphi} = d\varphi/dt$ ). A similar equation holds for atom II so that the total rotational kinetic energy of the molecule is

$$\epsilon_r = (\frac{1}{2}m_1 d_1^2 + \frac{1}{2}m_2 d_2^2)(\dot{\vartheta}^2 + \sin^2 \vartheta \dot{\varphi}^2) \quad (19.3)$$

The quantity  $m_1 d_1^2 + m_2 d_2^2$  is equal to the moment of inertia  $I$  of the molecule and, by elimination of  $d_1$  and  $d_2$ , can be brought to the form

$$I = \frac{m_1 m_2}{m_1 + m_2} d^2 \quad (19.4)$$

To obtain the law of distribution for the rotational degrees of freedom it is necessary to distinguish between the distribution of orientations, corresponding to the spatial distribution of the molecules in the former treatment, and the distribution of the velocities of rotation, corresponding to the velocities of translation in the former treatment.

Orientations which appear equally often are those in which the axis of the molecule sweeps out equally large cones, or those in which atom I describes equally large areas on the sphere of radius  $d_1$ . The probability of an orientation in which the colatitude is between  $\vartheta$  and  $\vartheta + d\vartheta$  and the longitude between  $\varphi$  and  $\varphi + d\varphi$  is proportional to  $\sin \vartheta d\vartheta d\varphi$ .

The distribution of rotational velocities needs a more extensive treatment. It will be recalled that the Maxwellian distribution function for translational velocity, as presented in Sections 7 and 8, is made up of independent factors, one for each degree of freedom. Grouped differently it consists first of a factor depending on the constants of the molecule and the temperature. This constant has such a value as to give the total number of molecules when the distribution function is integrated over all values of the velocities. In case of a molecule which can move in three dimensions, this factor was  $N_0(m/2\pi kT)^{3/2}$ . The last factor of the distribution function is the volume element of the three dimensional velocity space, and the middle factor is the expression  $e^{-(\epsilon/kT)}$ , where  $\epsilon$  means the total energy of the molecule. In the case of an infinitely high temperature this exponential function takes the value 1, and the relative

probability of different states is simply given by the relative size of the volume element  $d\omega = d\xi d\eta d\zeta$  of the velocity space, which in turn is determined by the limits specified for the velocity under consideration.

In a similar manner the probability that the rotational velocity lies in a certain limited range will first be proportional to the volume element in velocity space which gives this range. In a diatomic molecule there are two components of the rotational velocity as described before. Therefore, this volume element will be two dimensional; it will be the element of a "velocity surface." If for a given polar angle  $\vartheta$  the angular velocity about the polar axis has a value between  $\dot{\varphi}$  and  $\dot{\varphi} + d\dot{\varphi}$ , and simultaneously the angular velocity along the meridian has a value between  $\dot{\vartheta}$  and  $\dot{\vartheta} + d\dot{\vartheta}$  this surface element has the value  $d\dot{\vartheta} \sin \vartheta d\dot{\varphi}$ .

If the temperature were infinite, this would give the probability of the rotational velocity apart from a constant factor made up so as to give the total number of molecules correctly. If the temperature is finite it is a most probable analogy to introduce here too a factor  $e^{-\epsilon_r/kT}$  where  $\epsilon_r$  means the rotational energy of the molecule (Equation [19.3]). This procedure is suggested clearly because, in the case of translation, the factor  $e^{-\epsilon/kT}$  does not contain anything peculiar to translation but includes even the potential energy. However, a more complete demonstration can be given by continuing the reasoning which led to an exact proof of Maxwell's law for the velocity of translation (Section 14). Let it be assumed that there are two kinds of molecules, one of which can only rotate around a fixed center while the other can have only translational motion. By calculating the changes which occur in the distribution of both kinds due to collisions between the two, one can show in exactly the same manner as that of the foregoing treatment that Maxwell's law holds as well for rotation as for translation.

In order to complete the expression it is only necessary to introduce a constant factor to take care of the total number of molecules. The number of molecules having, at a given moment, an orientation of their axes between the angles  $\vartheta$  and  $\vartheta + d\vartheta$ ,  $\varphi$  and  $\varphi + d\varphi$  and, for their angular velocities, values between  $\dot{\vartheta}$  and  $\dot{\vartheta} + d\dot{\vartheta}$  and  $\dot{\varphi}$  and  $\dot{\varphi} + d\dot{\varphi}$ , is then found to be

$$N_0 A e^{-\frac{\epsilon_r}{kT}} d\dot{\vartheta} d\vartheta \sin \vartheta d\dot{\varphi} \sin \vartheta d\varphi \quad (19.5)$$

The constant  $A$  is evaluated in a manner exactly similar to that used in the case of pure translation. The total number of molecules is set equal to  $N_0$ . For the evaluation of the integral introduce  $\Theta = \dot{\vartheta}$ ,  $\Phi = \sin \vartheta \dot{\varphi}$  as the components of the angular velocity. Then the integral will take the form

$$N_0 = N_0 A \int_{-\infty}^{+\infty} e^{-\frac{I\Theta^2}{2kT}} d\Theta \int_{-\infty}^{+\infty} e^{-\frac{I\Phi^2}{2kT}} d\Phi \int_0^\pi \sin \vartheta d\vartheta \int_0^{2\pi} d\varphi \quad (19.6)$$

The integration over the angles  $\vartheta$ ,  $\varphi$  gives  $4\pi$ , the surface of a sphere of unit radius, the integration over the angular velocities is formally quite similar to

the integration over the translational velocity discussed previously, and leads to

$$(19.7)$$

This is equivalent to the two-dimensional translation case, the only difference being that the mass  $m$ , which is appropriate for the translational velocity, is replaced by the moment of inertia  $I$ , which is appropriate for rotation. Therefore, the final distribution formula for rotation takes the form

$$dN = N_0 \left( \sqrt{\frac{I}{2\pi kT}} \right)^2 e^{-\frac{I}{2kT}(\vartheta^2 + \sin^2 \vartheta \varphi^2)} d\vartheta \sin \vartheta d\varphi \frac{\sin \vartheta d\vartheta d\varphi}{4\pi} \quad (19.8)$$

The evaluation of the average kinetic energy can be written in exactly the same form as for the two-dimensional case of pure translation by using the previous substitution. Thus

$$\left( \sqrt{\frac{I}{2\pi kT}} \right)^2 \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \frac{I}{2} (\Theta^2 + \Phi^2) e^{-\frac{I}{2kT}(\Theta^2 + \Phi^2)} d\Theta d\Phi = 2 \frac{kT}{2} \quad (19.9)$$

which gives accordingly to each of the two degrees of freedom of rotation an energy  $\frac{1}{2}RT$  per mole and a contribution to the molar heat capacity  $\frac{1}{2}R$ , as would be the case for a degree of freedom of translation.

It will be seen from the following table that the molar heat capacities at constant volume of a number of the diatomic gases equal  $\frac{5}{2}R$ .

TABLE III<sup>1</sup>  
MOLAR HEAT CAPACITIES OF DIATOMIC GASES

	$T^\circ \text{K}$	$C_v$	
$\text{N}_2$ .....	293	4.984	Calculated value, $\frac{5}{2}R = 4.95$
	92	4.733	
$\text{O}_2$ .....	293	4.985	
	197	4.83	
	92	4.91	
$\text{CO}$ .....	291	5.006	
	93	4.758	

<sup>1</sup> K. Scheel and W. Huse, *Ann. Physik*, 40, 473 (1913).

However, there are also obvious deviations in both directions.

	$T^\circ \text{K}$	$C_v$
$\text{Cl}_2$	288	4.875
	199	4.379
	92	3.335
	289	6.39 <sup>2</sup>

<sup>2</sup> J. R. Partington, *Physik. Z.*, 15, 601 (1914).

The experimental values which are lower than predicted can only be explained by means of the quantum theory. The high values for chlorine, on the other hand, suggest the possibility that some of the degrees of freedom have not been taken into account. Now a molecular model such as has been employed—known as the “dumb-bell” model since the two atoms act like masses at the end of a rigid rod—can rotate about the line joining the two atoms as well as about the two perpendicular axes about which the moment of inertia is  $I$ . This was originally assumed by Boltzmann<sup>3</sup> but, as a matter of fact, no such rotation takes place. The quantum theory is again required to prove this statement. It is, however, merely a generalization of the fact that the rotation of a *single* atom need not be taken into account, because the moment of inertia about the axis of the molecule is merely the sum of the moments of inertia of the individual atoms.

On the other hand, it must be remembered that the line connecting the two atoms is not rigid. The two atoms can therefore vibrate with respect to each other without affecting the motion of the center of gravity of the molecule. This means that the displacements of the two atoms from their equilibrium positions must always be oppositely directed, the two being at the same instant either both inside or both outside the positions of rest. Furthermore, the two displacements must be inversely proportional to the masses, and therefore directly proportional to the distances from the center of gravity, so that the various configurations of the molecule are always geometrically similar. If the total displacement is  $X$ ,

$$X_1 = \frac{m_2}{m_1 + m_2} X; \quad X_2 = \frac{m_1}{m_1 + m_2} X \quad (19.10)$$

and there is obtained for the energy of vibration

$$\epsilon_v = \frac{m_1 m_2}{m_1 + m_2} \frac{1}{2} (\dot{X}^2 + 4\pi^2 \nu^2 X^2) \quad (19.11)$$

Thus the energy equation is identical with that for a single vibrating particle of mass  $m_1 m_2 / (m_1 + m_2) = \bar{m}$ . If the two masses are very different this fraction is approximately equal to the smaller mass, because the larger body is almost at rest. This “effective mass” enters all problems of relative motion such as planetary motion about the sun or rather about the common center of gravity (Section 4).

Consider now a diatomic molecule whose atoms can vibrate but whose center of gravity is fixed in space. In order to describe the state of this molecule completely it is necessary to know that the displacement at a given moment is between  $X$  and  $X + dX$ , and that the corresponding velocity is between  $\dot{X}$  and  $\dot{X} + d\dot{X}$ . The state of the molecule may be described by a state point on a surface of coordinates  $X$  and  $\dot{X}$ . Then the foregoing condi-

<sup>3</sup> L. Boltzmann, *Wien. Ber.*, 63, 397 (1871).

tions correspond to the requirement that the statepoints lie in the elementary area  $dX d\dot{X}$ .

The number of molecules fulfilling this requirement is

$$dN = N_0 A' e^{-\frac{\epsilon_p}{kT}} d\dot{X} dX = N_0 A' e^{-\frac{\bar{m} \dot{X}^2}{2kT}} d\dot{X} e^{-\frac{4\pi^2 \nu^2 \bar{m} X^2}{2kT}} dX \quad (19.12)$$

The factor  $A'$  is determined as before by putting the total number of molecules equal to  $N_0$ ,

$$\left. \begin{aligned} N_0 &= N_0 A' \int_{-\infty}^{+\infty} e^{-\frac{\bar{m}}{2kT} \dot{X}^2} d\dot{X} \int_{-\infty}^{+\infty} e^{-\frac{4\pi^2 \nu^2 \bar{m}}{2kT} X^2} dX \\ &= N_0 A' \sqrt{\frac{2kT}{\bar{m}}} \int_{-\infty}^{+\infty} e^{-u^2} du \sqrt{\frac{2kT}{4\pi^2 \nu^2 \bar{m}}} \int_{-\infty}^{+\infty} e^{-v^2} dv \end{aligned} \right\} \quad (19.13)$$

$$A' = \frac{1}{\pi \sqrt{\frac{2kT}{\bar{m}}} \sqrt{\frac{2kT}{4\pi^2 \nu^2 \bar{m}}}} = \frac{\nu \bar{m}}{kT} \quad (19.14)$$

The average energy per mole is then given by the equation

$$\begin{aligned} \bar{E}_v &= N_A A' \int \int \epsilon_v e^{-\frac{\epsilon_v}{kT}} d\dot{X} dX \\ &= N_A A' \left( \int_{-\infty}^{+\infty} \frac{\bar{m}}{2} \dot{X}^2 e^{-\frac{\bar{m}}{2kT} \dot{X}^2} d\dot{X} \int_{-\infty}^{+\infty} e^{-\frac{\bar{m} 4\pi^2 \nu^2 X^2}{2kT}} dX \right. \\ &\quad \left. + \int_{-\infty}^{+\infty} e^{-\frac{\bar{m}}{2kT} \dot{X}^2} d\dot{X} \int_{-\infty}^{+\infty} \frac{\bar{m}}{2} 4\pi^2 \nu^2 X^2 e^{-\frac{\bar{m} 4\pi^2 \nu^2 X^2}{2kT}} dX \right) \quad (19.15) \end{aligned}$$

which has exactly the same form as the formula for the average energy of pure translation of a two-dimensional gas,  $\dot{X}$  taking the place of  $\xi$  and  $2\pi\nu X$  of  $\eta$ . The first member in (19.15) represents the kinetic energy, the second the potential energy. The integration is then performed in a similar manner and leads to the value

$$\bar{E}_v = RT$$

where  $\frac{1}{2}RT$  is contributed by the average kinetic energy in the same way as it has been contributed by this kinetic energy in all the preceding cases, and  $\frac{1}{2}RT$  is contributed by the potential energy. It is well known that in the case of a vibrating system with elastic forces or of a simple pendulum, the average of the potential energy is equal to the average of the kinetic energy, each supplying half of the total energy. The contribution of the vibration to the specific heat is accordingly  $R$  calories per mole.

If the molecule is now permitted to have motions of translation and rotation besides vibration the formula giving the distribution law will be made up of independent factors, each referring to one degree of freedom, i.e., the number of molecules which lie at a certain moment in a volume element between

$x$  and  $x + dx$ ,  $y$  and  $y + dy$ ,  $z$  and  $z + dz$ ; the velocity components of which lie between  $\xi$  and  $\xi + d\xi$ ,  $\eta$  and  $\eta + d\eta$ ,  $\zeta$  and  $\zeta + d\zeta$  while, at the same time, their axes have an orientation given by the ranges of angles  $\vartheta$  to  $\vartheta + d\vartheta$ ,  $\varphi$  to  $\varphi + d\varphi$  and an angular velocity, the components of which lie between the limits  $\dot{\vartheta}$  and  $\dot{\vartheta} + d\dot{\vartheta}$ ,  $\dot{\varphi}$  and  $\dot{\varphi} + d\dot{\varphi}$ , and finally, a vibration of the atoms such that at the same moment the displacement of the atoms is between  $X$  and  $X + dX$ , while they move relatively to each other with a velocity between  $\dot{X}$  and  $\dot{X} + d\dot{X}$ ; it is given by

$$dN = N_0 \frac{dxdydz}{v} \sqrt{\frac{m}{2\pi kT}} e^{-\frac{m\xi^2}{2kT}} d\xi \sqrt{\frac{m}{2\pi kT}} e^{-\frac{m\eta^2}{2kT}} d\eta \sqrt{\frac{m}{2\pi kT}} e^{-\frac{m\zeta^2}{2kT}} d\zeta \\ \times \frac{\sin \vartheta d\vartheta d\varphi}{4\pi} \sqrt{\frac{I}{2\pi kT}} e^{-\frac{I\dot{\vartheta}^2}{2kT}} d\dot{\vartheta} \sqrt{\frac{I}{2\pi kT}} e^{-\frac{I\sin^2 \vartheta \dot{\varphi}^2}{2kT}} \sin \vartheta d\dot{\varphi} \\ \times 2\pi\nu \sqrt{\frac{m}{2\pi kT}} e^{-\frac{m4\pi^2\nu^2 X^2}{kT}} dX \sqrt{\frac{m}{2\pi kT}} e^{-\frac{m\dot{X}^2}{2kT}} d\dot{X} \quad (19.16)$$

Furthermore, the total average energy of a molecule is made up here by the sum of contributions of translation, rotation and vibration, just as in the case of a single atom it was made up of a sum of contributions from each degree of freedom of translation.

The justification for the integration to infinity in Equations (19.9) and (19.13) is the same as discussed after Equation (8.8), namely that due to the very marked decrease of the value of the exponential formula, it does not make any appreciable difference for the value of the integral if it is extended to a rather high upper limit or actually to infinity. The latter calculation is very much simpler than the former.

From Equations (8.28), (19.9) and (19.13) it is apparent that the total molar heat capacity at constant volume should be

$$\underbrace{\frac{3}{2}R}_{\text{Translation}} + \underbrace{\frac{2}{2}R}_{\text{Rotation}} + \underbrace{\frac{2}{2}R}_{\text{Vibration}} = \frac{7}{2}R \quad (19.17)$$

This value, however, is not attained by many diatomic gases at normal temperatures, the actual values being between  $\frac{5}{2}R$  and  $\frac{7}{2}R$ . The reasons for this can only be obtained from the quantum theory, as mentioned earlier.

(b) *Polyatomic Molecules*: The foregoing principles remain unchanged in the treatment of polyatomic gases, the only difference being a new, namely the third, axis of rotation so that the rotational heat capacity is  $\frac{3}{2}R$  if the molecule is not linear. There are, moreover, further possibilities for vibration.

In general, a molecule consisting of  $s$  atoms has  $3s$  degrees of freedom, as a point has three, and this number is not changed by any forces acting between the atoms, here considered as points. Of the  $3s$  degrees of freedom, three are those of translation and three those of rotation, if the atoms are not all arranged in a straight line. If they are all lying on one straight line (linear molecule), there are only two degrees of freedom of rotation. All the other degrees of



freedom must be those of vibrations, i.e.,  $3s - 5$  in a linear molecule,  $3s - 6$  in a nonlinear one. According to classical theory, if all the oscillations can be considered harmonic,  $C_v$  for a nonlinear polyatomic molecule should be <sup>4</sup>

$$\frac{3}{2}R + \frac{3}{2}R + (3s - 6)R = (3s - 3)R \quad (19.5)$$

However this is not the case. For example, the value of  $C_v$  for methane,  $\text{CH}_4$ , at  $15^\circ\text{C}$  is 6.49 cal. per deg. per mole. Since  $3R = 5.94$ , it is seen that the heat capacity is due to the translation and rotation and only slightly (0.55) to the vibration. Here again the anomaly can only be explained by the quantum theory.

With increasing temperature, the heat capacity of a polyatomic molecule increases in general, because the vibrational heat capacity becomes more and more classical.

(20) **Exchange of energy:** (a) *Translational Energy:* The translational energy is readily exchanged between molecules during the collision process according to Equation (8.30). A molecule with excessive velocity loses the excess substantially in a very few collisions, although the direction of motion partly persists after a single collision ("persistence of velocity" according to Jeans). Only in the case in which the mass of the colliding molecule is very different from that of the surrounding molecules does the equalization need many collisions.

(b) *Vibrational Energy. Absorption of Sound:* The rate of exchange of translational and vibrational energy makes itself felt in the propagation of high frequency sound waves. In a sound wave of intensity  $I$  (ergs/cm<sup>2</sup> sec) there occur pressure changes  $P$  given by

$$I = \frac{1}{2} V \kappa P^2 \quad (20.1)$$

where  $V$  is the velocity of sound and  $\kappa$  the compressibility. Since under normal circumstances the compression is nearly adiabatic, one has to use the adiabatic compressibility which is connected with the usual isothermal compressibility  $\kappa_{\text{iso}}$  by

$$\kappa_{\text{ad}} = \frac{C_v}{C_p} \kappa_{\text{iso}} = \frac{1}{\gamma p} \quad (20.2)$$

The first part of this equation applies to any fluid, the second half only to an ideal gas,  $\gamma$  being the ratio of the heat capacities and  $p$  the static pressure.

With the pressure variation  $P$  (supposed to be small compared with  $p$ ) there is connected a periodical temperature variation  $\Delta T$

$$\frac{\Delta T}{T} = \frac{\gamma - 1}{\gamma} \frac{P}{p} = \frac{R}{C_p} \frac{P}{p} \quad (20.3)$$

If a high frequency sound wave moves a distance  $x$  through a gas, there occurs an attenuation of the intensity given by  $e^{-2\alpha x}$ ;  $2\alpha \text{ cm}^{-1}$  is called the absorp-

<sup>4</sup> Deviation from Hooke's law and the consequent anharmonicity of the oscillations should in general increase the heat capacity further.

## THE KINETIC THEORY OF IDEAL GASES

tion coefficient for intensity,  $\alpha$  the absorption coefficient for amplitude. Part of this absorption coefficient  $\alpha$  was explained by Stokes and Kirchhoff<sup>1</sup> as due to viscosity and heat conduction. It follows from the equations of motion (17.3), (17.4), (17.5), that this classical part  $\alpha'$  of the absorption coefficient is<sup>2</sup>

$$\alpha' = \frac{8\pi^2\nu^2}{3V^3\rho} \left( \eta + \frac{3}{4} \frac{\gamma - 1}{c_p} \right) \quad (20.4)$$

where  $\nu$  is the sound frequency,  $V$  the sound velocity,  $\rho$  the density and  $c_p = C_p/M$  the specific heat per gram ( $M$  = molecular weight). This formula, valid for any liquid, can be simplified for ideal gases to

$$\alpha' = \frac{8\pi^2\nu^2}{3V^3\rho} \left[ 1 + \left( \frac{3R}{4C_p} \right) \left( \frac{M\lambda}{C_v\eta} \right) \right] \quad (20.5)$$

$M\lambda/C_v\eta$  being a pure number (see 31.11, 31.13). However, it is found that in almost all gases (argon being an exception) the actual absorption is larger than  $\alpha'$  as given by the classical formula (20.5).

Herzfeld and Rice<sup>3</sup> have explained the increased sound absorption by a slow exchange of internal and external energy. Jeans<sup>4</sup> had predicted the effect previously, but since, in 1904, no experimental test was possible, his investigation had been forgotten. The physical idea is as follows. As mentioned earlier, the pressure rise in a sound wave is accompanied by a temperature rise. If the temperature change is in phase with the density change, the effect is "wattless" and no work is done during a cycle. If the energy exchange is slow, the internal degrees of freedom will not take on the appropriate "temperature" immediately; the temperature change and, accordingly, the pressure change will lag behind the density change. Therefore, there exists a "watt component" (in electrical language) which will heat the gas and produce a corresponding loss of sound energy. The increased absorption is accompanied by dispersion, i.e., an increase of sound velocity with frequency.

The square of the sound velocity is given by

$$V^2 = \gamma \frac{RT}{M} = \left( 1 + \frac{R}{C_v} \right) \frac{RT}{M} \quad (20.6)$$

If at higher frequency only a part of the heat capacity  $C_v$  participates in the heat exchange, a given compression results in a larger temperature increase, larger pressure increase and therefore higher sound velocity.

<sup>1</sup> G. G. Stokes, *Cambr. Trans. Phil. Soc.*, **8**, 287 (1845); G. Kirchhoff, *Pogg. Ann.*, **134**, 177 (1868).

<sup>2</sup> See e.g., W. T. Richards, *Rev. Mod. Phys.*, **11**, 36 (1939); L. Bergmann, *Ultrasonics* (New York: John Wiley and Sons, 1938); 5th German edition, S. Hirzel, Zürich, (1949).

<sup>3</sup> *Phys. Rev.*, **31**, 691 (1928).

<sup>4</sup> *Dynamical Theory of Gases* (Cambridge University Press, 1904), pp. 228, 302 and Chapter XVI.

To obtain a formula <sup>5</sup> for the increased absorption, we introduce a relaxation time  $\tau'$ , needed to equalize the internal with the external degrees of freedom.<sup>6</sup> In the case mostly present in diatomic gases, where at room temperature only a small fraction of molecules has a vibrational quantum,  $\tau'$  is the lifetime of such an excitation. Since the vibration can lose energy only in a collision, and the interval between collisions is inversely proportional to the pressure, we have

$$\tau' = Z\tau_0/p \quad (20.7)$$

where  $\tau_0$  is the time between collisions for unit pressure, and  $Z$  the number of collisions needed on the average for deactivation.

We then write formally in Equation (20.6)

$$C_v = C' + C''(1 + i2\pi\nu\tau)^{-1} \quad (20.8)$$

where  $C'$  is the part of the heat capacity that is quickly adjusted and  $C''$  the part which has a relaxation time  $\tau'$ . An expression for a complex sound velocity  $V$  which includes both the usual sound velocity and the energy loss is then obtained. Straightforward calculation shows that

$$2(\alpha - \alpha') = \left( \frac{V}{V_0} \right)^2 \left[ \frac{C''R}{C_v(C_v - C'' + R)} \right] 4\pi^2\nu^2\tau(1 + 4\pi^2\nu^2\tau^2)^{-1} \quad (20.9)$$

with

$$= \left( 1 - \frac{C''}{C_v + R} \right) \tau' \quad (20.10)$$

where  $V_0$  is the sound velocity at low frequencies,  $C_v$  the static heat capacity.

If  $\alpha$  is plotted against the frequency, a curve starting from zero and reaching a plateau, without a maximum is obtained. If  $\alpha/\nu$  is plotted the curve has a maximum. For the purpose of evaluation, the best method is to plot  $\alpha/\nu^2$  against the frequency; the curve starts horizontally, and goes, at high frequency, to  $\alpha'$ . The value halfway between the low frequency value and  $\alpha'$  is reached at  $\nu = 1/2\pi\tau$ . On the other hand,  $V^2$  starts at low frequencies with  $V_0^2$  and reaches at high frequencies a plateau with the value  $(1 + R/C'')(1 + R/C_v)^{-1}V_0^2$ . The experimental curves, as function of  $\nu$ , follow the theory pretty well.

It has been found that if certain gases like  $H_2O$  are mixed in small percentage with others which have a large  $Z$  (i.e., long relaxation time) they diminish  $Z$  strongly, i.e., speed up deactivation and activation. Some results are recorded in Table IV.<sup>7</sup>

The theoretical connection of the law of force between molecules with the

<sup>5</sup> H. O. Kneser, *Ann. Physik*, 11, 761 (1931); 16, 360 (1933); A. J. Rutgers, *ibid.*, 16, 350 (1933).

<sup>6</sup> This is a slight simplification of the presentation given by K. F. Herzfeld, *J. Am. Ac. Soc.*, 13, 33 (1941).

<sup>7</sup> A. Eucken and L. Küchler, *Z. tech. Phys.*, 19, 66 (1938); L. Küchler, *Z. physik. Chem.*, B, 41, 199 (1935).

collision efficiency ( $1/Z$ ) has been discussed by Zener<sup>8</sup> and by Landau and Teller.<sup>9</sup>

(c) *Rotational Energy*: In hydrogen, the vibration is not excited at room temperature, because of the large value of  $\nu$ . Therefore an absorption in excess of  $\alpha'$  must be due to a delay in the exchange of rotational and translational energy. In other molecules this effect is swamped by the effect of the

TABLE IV  
NUMBER OF COLLISIONS ( $Z$ ) NEEDED FOR DEACTIVATION

Gas	Temperature, °C	$Z$
CO <sub>2</sub> .....	20	50,000
CO <sub>2</sub> + H <sub>2</sub> O.....	20	105
CO <sub>2</sub> .....	370	9,000
Cl <sub>2</sub> .....	20	34,000
N <sub>2</sub> O.....	20	7,500

delay in the exchange of vibrational energy, which has a much larger  $\tau'$ . For hydrogen, the anomalous dispersion has been discovered in the region of 10 mc for 1 atm pressure.<sup>10</sup> This gives a  $Z$  value of about 150.

### THE PHENOMENA OF FLOW AND CONDUCTION

The laws of viscosity, heat conduction and diffusion have afforded, in their time, much important evidence in support of the kinetic theory. Their fundamental features may be readily and simply deduced. However some of the developments of this section are not correct in so far as they do not take into account the disturbance of the distribution of the molecular velocities due to the flow and other factors. This omission can be avoided, in general, according to the methods outlined in Section 14, but the calculations are usually difficult.<sup>11</sup> In most cases such a detailed development does not affect the qualitative results of the simpler approximate method and has merely the effect of altering the numerical value of some coefficient. In a few instances, however, the more exact calculation shows that some coefficient is zero, which would otherwise

<sup>8</sup> *Phys. Rev.*, **37**, 556 (1931); **38**, 277 (1931).

<sup>9</sup> *Phys. Z. Soviet Union*, **10**, 34 (1936).

<sup>10</sup> E. S. Stewart, *Phys. Rev.*, **69**, 632 (1946); E. S. Stewart, J. L. Stewart, and J. C. Hubbard, *ibid.*, **68**, 231 (1945); J. E. Rhodes, Jr., *ibid.*, **70**, 932 (1946). A. van Itterbeck and P. Mariens, *Physica*, **4**, 609 (1937); A. van Itterbeck and L. Thys, *ibid.*, **5**, 889 (1938); A. van Itterbeck and R. Vermaelen, *ibid.*, **9**, 345 (1942). According to M. Kohler, *Z. Physik*, **125**, 715 (1949),  $Z$  is 1.27 for the translational energy and below 10 for the rotational energy in the case of N<sub>2</sub> and NH<sub>3</sub>.

<sup>11</sup> For details, see S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases* (London: Cambridge University Press, 1939); K. F. Herzfeld, in *Hand- und Jahrb. Chem. Physik*, Vol. 3, Sec. 2, IV (Leipzig: Akademische Verlags Ges., 1939); C. E. Curtiss and J. O. Hirschfelder, *The Kinetic Theory of Multicomponent Systems of Gases*, Univ. of Wisconsin, CF-727 (1947).

have been given a finite value. In such instances even the qualitative predictions of the inexact development are in error (e.g., Section 31, note 1).

(21) **Viscosity of Gases at Medium Pressures:** Consider a layer of gas of thickness  $d$  and extending to infinity on all sides. This layer is bounded by two plane surfaces parallel to the  $xy$ -plane. The lower surface ( $z = 0$ ) is stationary and the upper ( $z = d$ ) is moving in the direction of the  $x$ -axis with the velocity  $W_0$ . Experiment shows that in the stationary state the following conditions are fulfilled. The gas sticks to the two surfaces, if its density is not too small, so that at the bottom surface its velocity is zero and at the upper its absolute velocity is  $W_0$  in the  $x$ -direction. At the height  $z$  the velocity of the gas equals  $W_0 z/d$ . Each infinitely thin sheet of gas moves along the  $x$ -axis in its proper plane, the higher the sheet the greater being its velocity. This motion of the gas is governed by its internal friction. That is, each layer of the gas attempts to drag along with it the layer next below and to retard the layer immediately above. These frictional forces are also exerted on the enclosing surfaces. The force per square centimeter required to keep the bottom surface at rest or, which is the same thing, to keep the upper surface in uniform motion is given by

$$\eta \frac{\partial W}{\partial z} = \eta \frac{W_0}{d} \quad (21.1)$$

where  $\eta$  is the coefficient of viscosity and has the dimensions gram per centimeter per second. A kinetic explanation is now to be sought for the force which is exerted on each layer of the gas by the neighboring layers.

Throughout the present discussion the velocity of flow  $W$  will be defined as that velocity which must be subtracted from the  $x$ -component of the total velocities of the molecules in order that the remaining velocities shall be distributed according to Maxwell's law. The remaining velocities will accordingly define the temperature.<sup>1</sup>

Consider any layer at the height  $z$ , in which the velocity of flow  $W = W_0 z/d$ . The friction force exerted in the  $x$ -direction on this layer may be determined by calculating the amount of momentum in the  $x$ -direction transported upward in unit time through  $1 \text{ cm}^2$  of the layer. It will again be assumed at first as in Section 1 that one third of all the molecules are moving in the vertical direction. Of these, one half are moving upwards and the other half downwards. If the number of molecules per cubic centimeter is designated, as usual, by  $N_A/V$ , there are  $\frac{N_A}{6V} |\bar{w}|$  molecules<sup>2</sup> crossing each square centimeter of the upper boundary of the layer per second coming from above. Aside from their thermal velocity these molecules possess an additional velocity in the  $x$ -direction,  $W_+$ , which is greater than that possessed by the molecules of the layer under consideration. This is so because the last opportunity that each molecule coming from above had to adjust its velocity was at its last collision, which was, on

<sup>1</sup> J. C. Maxwell, *Phil. Mag.*, 19, 31 (1860). This is not quite correct; Sections 14, 15.

<sup>2</sup>  $|\bar{w}|$  is the magnitude of the average molecular velocity.

the average, at a distance equal to one mean free path  $\Lambda$  above the layer  $z$ . On the average, therefore, each molecule assumed at its last collision the velocity of flow prevailing in the layer in which the last collision occurred, namely, the velocity of the layer  $z + \Lambda$ . This velocity equals

$$W_+ = W + \frac{\partial W}{\partial z} \Lambda \quad (21.2)$$

The higher terms of this Taylor's series are omitted, since without a linear velocity gradient momentum would accumulate (see Equation (21.4)). The molecules coming from above therefore bring into the layer an average momentum in the  $x$ -direction equal to  $\frac{N_A}{6V} |\bar{w}| m W_+$ , since each molecule carries an  $x$ -component of momentum of  $m W_+$  on the average.

Similarly the molecules coming upwards from the layer below have a velocity equal to

$$W_- = W - \frac{\partial W}{\partial z} \Lambda \quad (21.3)$$

because they come from a layer lower by the distance  $\Lambda$ . They carry upward an  $x$ -component of momentum equal to  $\frac{N_A}{6V} |\bar{w}| m W_-$ . The net flow of momentum through the layer is therefore

$$\frac{N_A}{6V} |\bar{w}| m (W_+ - W_-) = \frac{N_A}{3V} |\bar{w}| m \Lambda \frac{\partial W}{\partial z} \quad (21.4)$$

This excess momentum is due to the fact that molecules moving downward have a larger  $x$ -component of velocity than those coming from beneath.

This downward flow of momentum along the  $x$ -axis corresponds to a force acting on the lower limiting surface, the value of this force per square centimeter being  $\frac{N_A}{3V} |\bar{w}| m \Lambda \frac{\partial W}{\partial z}$ . Upon comparison with Equation (21.1) it is seen that

$$\eta = \frac{N_A}{3V} |\bar{w}| m \Lambda = \frac{1}{3} M |\bar{w}| c \Lambda \quad (21.5)$$

where  $M$  is the molecular weight and  $c$  is the number of moles per cubic centimeter. Before proceeding to the discussion of this equation the fundamental facts may be summarized as follows. The effect experienced by any layer of the gas due to the layer immediately above it is caused by the downward migration of molecules from the upper layer. These molecules are moving faster in the direction of the  $x$ -axis than are the molecules of the first layer. Upon collision, the differing amounts of momentum are exchanged so that the first layer is accelerated in the  $x$ -direction. On the other hand, the slower molecules coming upwards from the layer immediately below the layer under

consideration tend to retard the latter. In the stationary state the acceleration and retardation compensate each other. The excess components of velocity in the  $x$ -direction are changed by collisions to velocities in which no direction is favored; the mass motion of the molecules is partly converted into thermal motion and, as a result of its viscosity, the gas is warmed.<sup>3</sup> The force exerted upon the lower surface is caused by the fact that the molecules reaching it still have an excess momentum in the  $x$ -direction which they give up to the plate upon collision. After the subsequent reflection they retain only their thermal velocity. This force caused by collisions is along the  $x$ -axis and therefore in the plane of the plate, and must be balanced by an external force to preserve equilibrium. There is a point to be noted in this connection which will be brought up later (Section 24).

To return to Equation (21.5), it is seen that the viscosity of a gas is *independent of the density*, since  $\Lambda$  is inversely proportional to  $c$ . This unexpected result was first deduced from the theory by Maxwell. After the experimental confirmation by Kundt and Warburg it became one of the strongest pieces of evidence in support of the kinetic theory<sup>4</sup> (Table V). The reason for this

TABLE V  
APPARENT \* VISCOSITY OF AIR AT DIFFERENT PRESSURES,  $t = 15^\circ\text{C}$

$p$ , mm Hg	$\eta/\eta_{750 \text{ mm}}$	$\Lambda$ (mm)
750	1	$6.0 \times 10^{-5}$
380	1.01	$1.2 \times 10^{-4}$
20.5	1.004	$2.2 \times 10^{-3}$
2.4	0.978	$1.9 \times 10^{-2}$
1.53	0.956	0.030
0.63	0.908	0.073

Distance between the plates = 1.967 mm

\* "Apparent" because the decrease at low pressures is caused by slippage.

independence of density is that, although the number of molecules acting as carriers of momentum is increased by increase in the density, at the same time the effect of each carrier is diminished, since each one brings in a smaller excess (or deficiency) of momentum because it comes from a shorter distance.

The viscosity of air increases<sup>5</sup> by 1 per cent if the pressure is raised to 35

<sup>3</sup> G. Jäger, *Winckelmanns Handb. d. Physik*, Vol. III, p. 139 f., (2d ed., Leipzig), 1906.

<sup>4</sup> O. E. Meyer, *Pogg. Ann.*, 125, 177 (1865); 127, 253, 353 (1866); 148, 1 (1873); O. E. Meyer and Springmühl, *Pogg. Ann.*, 148, 526 (1873); Clerk Maxwell, *Phil. Trans. Roy. Soc.*, 156, 249 (1866); W. Crookes, *ibid.*, 172, 387 (1881).

<sup>5</sup> A. G. Nasini and G. Partonesi, *Gazz. Chim. Ital.*, 63, 821 (1933); see also W. Schugajew, *Phys. Z. Soviet Union*, 5, 659 (1934) for  $\text{H}_2\text{O}$ ; E. W. Comings and R. S. Egly, *Ind. Eng. Chem.*, 33, 1224 (1941) for  $\text{CO}_2$  and  $\text{C}_2\text{H}_4$ ; A. S. Smith and G. G. Brown, *ibid.*, 35, 705 (1943) for  $\text{C}_2\text{H}_6$  and  $\text{C}_3\text{H}_8$ ; W. L. Sibitt, G. A. Hawkins, and H. L. Solberg, *Trans. Am. Soc. Mech. Eng.*, 65, 401 (1943) for  $\text{N}_2$ ; S. N. Naldrett and O. Maass, *Canad. J. Res.*, B, 18, 322 (1940) for  $\text{CO}_2$  in critical region; S. G. Mason and O. Maass, *ibid.*, p. 128, for  $\text{C}_2\text{H}_4$  in critical region; G.

atm and by about 25 per cent at 200 atm. This is due to deviations from ideal gas behavior.

For isotopes, the molecules of which have the same size and exert the same forces, the only difference is the mass  $M$ , which enters in Equation (21.5) as an explicit factor and, for a given temperature, appears in the form  $M^{-1/2}$  in the thermal velocity, so that  $\eta$  should be proportional to  $\sqrt{M}$ . Therefore the coefficients of viscosity for  $D_2$  and  $H_2$  should have the ratio  $\sqrt{4}:\sqrt{2} = 1.41$ . This is confirmed for room temperature <sup>6</sup> while the ratio falls to 1.24 at liquid helium temperatures. Van Itterbeek and Grande <sup>6a</sup> ascribe this to the fact that at low temperatures  $\Lambda$  for  $H_2$  is larger than for  $D_2$ , and confirm this by measuring the thermal effusion (see Section 35) in a condition where this is affected by the ratio of tube diameter to  $\Lambda$ . From results of this same method, they conclude that even at 582°K,  $\Lambda$  for  $H_2$  is larger than  $\Lambda$  for  $D_2$  by 3 per cent. No theory has been worked out for this latter phenomenon.

The coefficient of viscosity should change with the temperature, according to Equation (21.5), only in so far as  $|\bar{w}|$  changes with the temperature. In other words, it should be proportional to  $\sqrt{T}$  (because the velocity of transport is increased). Actually it increases with the temperature more rapidly than this. It may therefore be concluded that the mean free path increases with the temperature, as discussed in Section 13.

The agreement of the formula

$$\eta = A \frac{T^{1/2}}{1 + \frac{T}{C}} \quad (21.6)$$

with experiment is doubtlessly good within a limited range, but for a wide range of temperatures (from room temperature up) the results are disputed. Brémont <sup>7</sup> has covered a very wide interval of temperatures in his measurements for air (18 to 1134°C) and  $CO_2$  (19 to 1052°C). He finds good agreement with (21.6) as is shown in Table VI, which is an excerpt of his data,  $C$  being taken as 119.4.

Similarly, Braune, Basch and Wentzel <sup>8</sup> find good agreement for Hg vapor (218 to 610°C), Trautz and Zink <sup>9</sup> for air,  $N_2$ ,  $O_2$ , A (16 to 825°C). Licht and

Kellström, *Ark. Mat., Astr. Fys.*, **27A4**, N23 (1941) for precision measurements on air up to 30 atm. For the theory, see, S. Chapman and T. G. Cowling, *The Mathematical Theory of Non Uniform Gases*, Chapter 16, (London: Cambridge University Press, 1939).

<sup>6</sup> H. C. Torrey, *Phys. Rev.*, **47**, 644 (1935); I. Amdur, *J. Am. Chem. Soc.*, **57**, 588 (1935); A. B. Cleave and O. Maass, *Canad. J. Res.*, **12**, 57 (1935); A. van Itterbeek and A. Claes, *Physica*, **5**, 938 (1938); A. van Itterbeek and O. van Paemel, *ibid.*, **7**, 265 (1940). The ratio of  $\eta$  for  $CD_4$  and  $CH_4$  is close to the theoretical one; A. van Itterbeek, *ibid.*, p. 831.

<sup>6a</sup> *Physica*, **13**, 289, 422 (1947).

<sup>7</sup> *Compt. rend.*, **196**, 1472 (1933).

<sup>8</sup> *Z. physik. Chem.*, **137**, 176, 447 (1928).

<sup>9</sup> *Ann. Physik*, **7**, 427 (1930).



Stechert<sup>10</sup> have found good agreement with the data in the literature for many gases.

On the other hand, Braune<sup>11</sup> and his coworkers have represented their results for air by taking different values of  $C$  in different regions (123.6 between 17°C and 477°C; 200 above 377°C). Similarly Binkley<sup>12</sup> interprets Trautz's data with a variable  $C$ . Chemically active gases and some organic vapors also give irregular results, which might be due to experimental error. Near the critical temperature, Trautz<sup>13</sup> finds  $\eta$  proportional to  $T$ .

TABLE VI  
VISCOSITY OF AIR AS FUNCTION OF THE ABSOLUTE TEMPERATURE

$T^\circ\text{K} \dots \dots \dots$	291	502	607	739	838	1023	1196	1307	1407
$\eta \times 10^7$ (exp.) . .	1827	2638	3123	3501	3750	4263	4643	4906	5206
$\eta \times 10^7$ (theor.)	1824	2729	3104	3528	3820	4318	4743	4996	5215

Ribaud and Vasilescu<sup>14</sup> have investigated the viscosity over a very wide temperature range and find the Sutherland formula to represent their measurements only if  $C$  is taken as varying somewhat with  $T$ . Their results are shown below.

Gas	Air	Ne	A	CO <sub>2</sub>
$C$ at 275°K	113	110	142	254
$C$ at 1900°K	124	120	168	307

However, they use a metal capillary wound into a spiral, which, according to Partington,<sup>15</sup> might distort the results.

Other precision measurements of viscosity in the range of 100°K to 300°K are due to Johnston<sup>15a</sup> and his collaborators, while Vasilescu and Rammner and Breitling<sup>15b</sup> have extended the measurements to 1500°K.

At very low temperatures the behavior is different and will be treated later.

All the quantities of Equation (21.5) are known with the exception of  $\Lambda$ . (The numerical factor 1/3 is not quite correct, see the following paragraph.) Viscosity measurements may therefore be used to calculate the value of the mean free path, and from this the diameter of the molecule (Equation [11.2]). Thus Smith<sup>16</sup> has shown that nitrogen has the same viscous properties as carbon monoxide. Each of these gases is diatomic and each has the same molecular weight and number of electrons, i.e., they are isosteres. The same

<sup>10</sup> W. Licht, Jr. and D. G. Stechert, *J. Phys. Chem.*, **48**, 23 (1944).

<sup>11</sup> *Loc. cit.*

<sup>12</sup> *Ann. Physik*, **9**, 839 (1931).

<sup>13</sup> *Ibid.*, **10**, 263 (1931); **11**, 190 (1931); **15**, 198 (1932); **16**, 751, 865 (1933).

<sup>14</sup> *Compt. rend.*, **208**, 884 (1939).

<sup>15</sup> *Physik. Z.*, **34**, 289 (1933).

<sup>15a</sup> H. L. Johnston and K. E. McCloskey, *J. Phys. Chem.*, **44**, 1038 (1939); H. L. Johnston and E. R. Grilly, *ibid.*, **46**, 948 (1942).

<sup>15b</sup> *Die Wärme*, **60**, 620 (1937).

<sup>16</sup> *Proc. Phys. Soc.*, **34**, 155 (1922).

similarity holds for carbon dioxide and nitrous oxide which also show the same viscosity. Rankine<sup>17</sup> has compared the molecular dimensions of carbon oxy-sulphide obtained from viscosity measurements with dimensions calculated from model considerations.<sup>18</sup>

According to Enskog and Chapman<sup>19</sup> the accurate formula for elastic spheres is

$$\eta = \frac{5}{16} \times 1.016 \sqrt{\frac{RTM}{\pi}} \frac{1}{N_A d^2} \quad (21.7)$$

or with 
$$\Lambda = \frac{1}{\sqrt{2\pi c N_A d^2}} \quad (21.8)$$

and 
$$|\bar{w}| = 2 \sqrt{\frac{2RT}{\pi M}} \quad (21.9)$$

$$\eta = 0.499cM |\bar{w}| \Lambda \quad (21.10)$$

The general expression is

$$\eta = \frac{5}{8} kT / \Omega_{(2)}^{(2)} \quad (21.10a)$$

multiplied by a small correction function which varies between 1.000 and 1.008. If the elastic spheres attract each other according to the law of force,  $F = -An/r^{n+1}$ , Sutherland's constant (Equation [13.10]) becomes

$$C = \frac{217}{615} \frac{A}{kd^n} \beta \quad (21.11)$$

where  $\beta$ , the numerical coefficient, has the following values:

$n = 2$	3	4	6	8
$\beta = 0.701$	0.636	0.587	0.517	0.467

Finally, if the molecules are assumed to be force centers repelling each other so that the potential energy is proportional to  $A/r^n$ , instead of elastic spheres, Equation (21.6) is to be multiplied by the term  $3(2kTn/A)^{2/n}$  and also by a numerical factor dependent on  $n$ .<sup>20</sup>

The result for the repulsive forces is easily interpreted. The potential energy of repulsion is  $A/r^n$ . If a molecule approaches another one with the relative velocity  $w$  head on, it will be stopped when its whole (relative) kinetic energy has been changed into potential energy. If this distance is called  $r_0$ , it follows that

$$A/r_0^n = \bar{m}w^2/2 \quad (21.12)$$

<sup>17</sup> *Phil. Mag.*, **44**, 292 (1922).

<sup>18</sup> Cf. also E. Mack, Jr., *J. Am. Chem. Soc.*, **47**, 2468 (1925).

<sup>19</sup> D. Enskog, *Physik. Z.*, **12**, 56, 533 (1911); *Ark. Math. Astr. Phys.*, **16**, No. 16, 1922. S. Chapman, *Phil. Trans. Roy. Soc.*, **216**, 279 (1916); **217**, 115 (1917).

<sup>20</sup> For the evaluation of some of the integrals occurring in the expressions for viscosity, etc., as a function of the exponent  $n$  of the law of force see S. Chapman, *Mem. Proc. Manchester Lit. Phil. Soc.*, **66**, 1 (1922) and J. Hirschfelder, Section 17.

where  $\bar{m}$  is the effective mass. Since  $r_0$  plays a role analogous to the size  $d$  of the hard sphere in (21.7),  $\eta$  is proportional to  $\pi r_0^2$ , which is a kind of scattering cross-section. As  $mw^2/2$  is on the average proportional to  $T$ ,  $r_0$  is proportional to  $T^{-1/n}$  and  $r_0^{-2}$  to  $T^{2/n}$ .

Actually, the molecules have both attractive and repulsive forces. Lennard-Jones<sup>21</sup> and Hassé and Cook<sup>22</sup> have done a great deal of work on the evaluation of the corresponding formulae.

Recently, Hirschfelder and his coworkers have devoted a great deal of work to the problem,<sup>22a</sup> as mentioned at the end of Section 17. The formula they use as interaction energy contains two constants,  $\epsilon$  and  $r_0$ , which they determine from the viscosity of the gas and its temperature dependence. They have tabulated these force constants for a number of gases. The following table compares their results with those of the Sutherland formula and with experiment, the experimental values at  $T = 200$  and  $300^\circ$  having been used to find the constants.

TABLE VIa  
VISCOSITY OF NITROGEN,  $10^7 \eta$

$T^\circ\text{K}$	Exp.	Hirschfelder	Sutherland $C = 101.1$
100	698	687	686
120	826	820	820
160	1068	1070	1069
200	1295	1296	(1295)
240	1505	1503	1503
300	1786	1785	(1786)
500	2657	2570	2564
1000	4011; 4066	4068	3960
1200	4452; 4613	4554	4405
1500	5050; 5247	5268	5002

In view of the very different assumptions, it is rather astonishing that the simple Sutherland formula gives such good agreement.

To arrive at a more systematic comparison, Hirschfelder's temperature function ( $V/W_{(2)}^{(2)}$ ) was compared with the Sutherland equation (Table VIb). The values for  $kT/\epsilon$  equal to 1 and to 3 were chosen (they appear in brackets in Table VIb) to give the best fit. It was found that one has to take

$$C = 1.0889 \frac{\bar{v}}{k}$$

<sup>21</sup> *Proc. Roy. Soc., A*, **106**, 441 (1924); **107**, 157 (1925); J. E. Jones and W. R. Cook, *ibid.*, **112**, 214 (1926).

<sup>22</sup> *ibid.*, **125**, 196 (1929).

<sup>22a</sup> J. O. Hirschfelder, R. B. Bird and E. L. Spotz, *J. Chem. Phys.*, **16**, 958 (1948); *Chem. Rev.*, **44**, 205 (1949). Tables with more details and nomographs have been given by LeRoy A. Bromley, UCRL Report 525, Tech. Inf. Div., ORE, AEC Oak Ridge, Tenn.

The values listed under "Sutherland" are then calculated from the expression

$$\frac{1.3162}{1 + \frac{C}{T}}$$

where the factor 1.3162 is introduced due to the Hirschfelder's choice of constants, so that (21.6) would read

$$\eta = \frac{A}{1.3162} T^{\frac{1}{2}} \frac{1.3162}{1 + \frac{C}{T}}$$

TABLE VIb  
COMPARISON OF SUTHERLAND AND HIRSCHFELDER EQUATIONS

$kT/\epsilon$	Sutherland	Hirschfelder
0.3	0.2843	0.3596
0.5	0.4142	0.4432
0.75	0.5368	0.5432
1	(0.6301)	0.6301
1.25	0.7035	0.7023
1.5	0.7626	0.7613
2	0.8522	0.8523
2.5	0.9168	0.9172
3	(0.9657)	0.9657
4	1.035	1.036
5	1.081	1.085
10	1.187	1.222
50	1.288	1.550
100	1.292	1.714
400	1.310	2.095

It is seen that the agreement between the two expressions is better than 2 in one thousand in the range of  $T$  between  $C$  and  $4C$ , and better than 4 per cent for  $T$  between  $0.75C$  and  $C$  and for  $T$  between  $4C$  and  $10C$ . For values below  $T$  equal  $C$ , Sutherland's equation gives too small a viscosity, i.e., overestimates the effect of the attractive forces. For values of  $T$  above  $4C$  and particularly above  $10C$  where the effect of the attractive forces is small, the Hirschfelder equation shows a much stronger increase in viscosity. This is obviously due to the fact, that with increasing kinetic energy the molecules show themselves "softer," in agreement with the form of the repulsive energy, than is assumed by the "hard" sphere model, and therefore have a decreasing cross section. This is in agreement with Bromley's statement (l.c.), that for large  $kT/\epsilon$ ,  $V/W_{(2)}^{(2)}$  may be represented as being proportional to  $T^{0.145}$ , which, according to the text following Equation (21.12) would correspond to molecules having a repulsive potential proportional to  $r^{-13.8}$ . In the range where the two

formulas for the temperature dependence agree one has to choose in Equation (21.7), after multiplication with  $(1 + C/T)^{-1}$

$$d = \left( \frac{\sqrt{2} \cdot 1.3162}{2} \right)^{\frac{1}{2}} r_0 = 0.9647 r_0$$

where  $r_0$  is the quantity listed by Hirschfelder.

It might be mentioned here that in the exact theory of viscosity, as developed by Enskog and Chapman, not only the momentum transfer through collisions, as pictured in the elementary way, has to be considered, but also that momentum transfer which occurs when one molecule is deflected by the forces of another at greater distance. Because of the conservation of motion of the two molecules combined, the deflecting molecule shows recoil, which amounts to transfer of momentum from the deflected to the deflecting molecule.

**(22) Low Temperatures. Quantum Theory:** The only gases that can be investigated at very low temperatures are  $H_2$ , He, Ne and A. It has long been known that they behave differently there than is generally the case in the high temperature range. Trautz<sup>1</sup> has used  $T^n$  instead of  $T^{\frac{1}{2}}$  in (21.6). Hydrogen has been measured between 575°K and 14°K, the low temperature measurements having been repeated by van Itterbeek and Claes.<sup>2</sup> At 575°K,  $\eta$  has 1.626 times the value at 273°K. Between 575°K and 195°K the temperature dependence of  $\eta$  can be represented about equally well with a Sutherland formula ( $C = 71.7$ ), and an expression  $(T/273)^{0.685}$ . For low temperatures (at 14°K,  $\eta$  has about  $\frac{1}{12}$  the value at 273°K) the experimental data lie between the two expressions (Sutherland's formula giving the lower values, i.e., the greater variation). For argon,  $\eta$  is found proportional to  $T^{0.883}$  at low temperatures.<sup>3</sup>

However, it would be unjustified to draw conclusions from classical theory for the light gases. From quantum theory, we know that there is associated with each particle a de Broglie wave of wave length  $h/mv$ . If we use for  $w$  the value given by

$$\frac{1}{2}mv^2 = \frac{3}{2}kT \quad (22.1)$$

we have for the de Broglie wavelength about  $25.2M^{-\frac{1}{2}}T^{-\frac{1}{2}}$  Ångström ( $10^{-8}$  cm), i.e., for  $M = 2$ ,  $T = 18^\circ\text{K}$ , it is about 4.2 Å, and for  $M = 20$ ,  $T = 300^\circ\text{K}$ , it is about 0.3 Å.

It is known from optics that whenever the wavelength of light is small compared with a material object on which the light falls (mirror or lens) we can use geometrical optics and construct the image with the help of rays. Diffraction phenomena remain inconspicuous, restricted to the edges of the mirror or lens. On the other hand, if the wavelength is comparable with the object, geometrical optics is misleading, diffraction phenomena become promi-

<sup>1</sup> M. Trautz and R. Zink, *Ann. Physik*, 7, 427 (1930).

<sup>2</sup> *Loc. cit.*; cf. W. H. Keesom and P. H. Keesom, *Physica*, 7, 29 (1942).

<sup>3</sup> A. van Itterbeek and O. van Paemel, *ibid.*, 5, 1009 (1938); 7, 265, 273 (1940) for Ne, He;  $O_2$ ,  $H_2$ ,  $D_2$ .

nent, and "wave optics" is required. Similarly, if a gas atom is scattered by an object (another gas atom) this process can be treated by classical mechanics, which describes the motion of a particle by a definite path, i.e., something analogous to the rays of geometrical optics, so long as the de Broglie wavelength is short compared to the dimensions of the scatterer, i.e., short compared to a few Å. If, however, it is comparable to it, the description of the process by the motion of a particle along a definite path is to be replaced by the wave picture.

We now consider a plane parallel wave, representing a molecular ray of incoming particles, as falling on a scattering particle, which, to simplify the problem, is considered fixed in space. As the incoming particle and the scatterer interact through forces, the kinetic energy of the incoming particle changes from place to place. A change in kinetic energy, however, means a change in velocity and, consequently, of de Broglie wavelength. The scatterer acts therefore in the wave picture in the same way as a small region of different refractive index would act in optics. The result is the appearance of a scattered wave going out in all directions from the scatterer. The intensity of the scattered wave in any particular direction is proportional to the number of particles scattered in that direction.

The problem has been treated by Mohr and Massey<sup>4</sup> for helium and hydrogen. The formula for the viscosity is still

$$\eta = \left(\frac{5}{16}\right) 1.016 \sqrt{MRT\pi/N_A}/Q \quad (22.2)$$

but the classical scattering cross-section  $Q = \pi d^2$  is replaced by a quantum theoretical cross-section, in which a proper average for the different velocities present in the Maxwell distribution has to be taken.

The calculation has been made for helium by the same authors for the following alternatives:

- (a) Helium atoms are hard spheres of diameter 2.1 Å.
- (b) They act upon each other with the interaction energy calculated by Slater and Kirkwood from the electronic structure.

The results are given in Table VII which contains in the third column the results found with  $\eta \propto \sqrt{T}$  which would correspond classically to hard spheres. It is seen that the quantum theoretical values for hard spheres fit best.

Itterbeck and Keesom<sup>5</sup> have extended the measurements down to 1.64°K. These have been compared with the theory by de Boer,<sup>6</sup> who has extended the quantum treatment to low temperatures using a potential energy function of the form (see [17.9])

$$14.03 \times 10^{-16} \left[ \left( \frac{d}{r} \right)^{12} - \left( \frac{d}{r} \right)^6 \right] \text{ ergs,} \quad d = 2.56 \text{ Å}$$

<sup>4</sup> *Proc. Roy. Soc., A*, 141, 434 (1933); 144, 188 (1934); E. A. Uehling and G. E. Uhlenbeck, *Phys. Rev.*, 43, 552 (1933); E. A. Uehling, *ibid.*, 46, 917 (1934).

<sup>5</sup> *Physica*, 5, 257 (1939).

<sup>6</sup> *Ibid.*, 10, 348 (1943).

The value of  $\eta/\sqrt{T}$  rises steeply from 0°K, has a maximum at a small fraction of a degree and then rises slowly.

There exists in quantum theory a new effect, which has already been taken into account in the preceding calculations. In classical theory, if a particle A and a particle B collide and then rebound, one can always see which of the

TABLE VII  
VISCOSITY OF HELIUM IN  $10^{-6}$  ABSOLUTE UNITS

T°K	$\eta$ (exp.)	$\eta$ (classical)	$\eta$ (according to a)	$\eta$ (according to b)
294.5	199.4	200	185	213
273.1	187.0	193	177	—
250.3	178.8	184	169	—
203.1	156.4	167	150	165
170.5	139.2	152	135	—
88.8	91.8	110	92	98
75.1	81.5	101	81.5	—
20.2	35.03	52	35.5	43
15.0	29.46	45	30	36
4.23	12.77	24	—	—

rebounding particles is A and which B. In quantum theory, that is impossible, if A and B are of the same kind; therefore the probability of scattering is doubled <sup>7</sup> if the particles are of the same kind (indistinguishable) compared to the case where they are not alike but very similar, as each rebounding particle might be either A or B.

Halpern <sup>8</sup> pointed out that "same kind" in the above description has to be taken very literally. Two molecules in different states of rotation or with different orientation of the nuclear spins are to be taken as different. It follows that at low temperature when most molecules are in one or two rotation states there is a considerable chance to collide with a molecule of the same kind. At high temperature, where they are distributed over a great number of rotation states, the chance of meeting a particle of the same kind is very small. This effect means an increase in  $\eta$  with increasing temperature.

Halpern calculated for hydrogen, considered as consisting of hard spheres, the following relative values for  $\eta$  in dependence on the amount of para-hydrogen. The values are for 273°K and are relative to a gas which has only molecules of the same kind.

<sup>7</sup> The physical reason for this distinction is that in classical theory we can continuously observe a particle and follow it on its course through a collision. This is impossible in quantum theory. To put it differently, light of long wave-length must be used for observations so as not to disturb the collision through a simultaneous Compton effect with a light quantum. But then we observe, as the picture of the particle, only an optical diffraction disk made by the particle. In collision, the two disks merge, and when they separate, it is impossible to know to which original particle each disk belongs.

<sup>8</sup> O. Halpern and E. Gwathmey, *Phys. Rev.*, 52, 944 (1937).

Para-hydrogen (per cent)...	100	95	43	25 (equilibrium)
Relative $\eta$ .....	1.033	1.035	1.047	1.049

(23) **The Viscosity of Gaseous Mixtures:** The viscosity of gaseous mixtures is given by a rather complicated relation, but the approximate calculation may be carried through exactly as in the case of a simple gas. Thus the transport of momentum takes place in part through  $N_A c_1$  molecules of the first kind and partly through  $N_A c_2$  molecules of the second kind, etc. The molecules I have a free path  $\Lambda_1$  and so forth. There is obtained in this manner the relation

$$\eta = \frac{1}{3} [c_1 |\bar{w}_1| m_1 \Lambda_1 + c_2 m_2 |\bar{w}_2| \Lambda_2 + \dots] N_A \quad (23.1)$$

If there are only two components in the mixture this becomes, upon inserting the values of  $\Lambda_1, \Lambda_2$  given by (11.15) ( $d = (d_1 + d_2)/2$ ),

$$\eta = \frac{2\sqrt{2}}{3} \sqrt{\frac{RT}{\pi}} \frac{1}{N_A} \left( \frac{c_1 \sqrt{M_1}}{\pi \sqrt{2} c_1 d_1^2 + \pi c_2 d^2} \sqrt{\frac{M_1 + M_2}{M_2}} + \frac{c_2 \sqrt{M_2}}{\pi \sqrt{2} c_2 d_2^2 + \pi c_1 d^2} \sqrt{\frac{M_1 + M_2}{M_1}} \right) \quad (23.2)$$

$$= \frac{\eta_1}{1 + \frac{c_2}{c_1} \left(\frac{d}{d_1}\right)^2 \sqrt{\frac{M_1 + M_2}{2M_2}}} + \frac{\eta_2}{1 + \frac{c_1}{c_2} \left(\frac{d}{d_2}\right)^2 \sqrt{\frac{M_1 + M_2}{2M_1}}}$$

A formula of the type

$$\eta = \frac{\eta_1}{1 + \frac{c_2}{c_1} \beta_1} + \frac{\eta_2}{1 + \frac{c_1}{c_2} \beta_2} \quad (23.3)$$

has been obtained by Sutherland<sup>1</sup> with the aid of simplifying assumptions but taking into account his temperature correction. However, the same has been done independently by Thicssen<sup>2</sup> with another meaning for  $\beta$ . These formulae are in good agreement with the experimental data.<sup>3</sup>

On the other hand the relation

$$\frac{\beta_1}{\beta_2} = \frac{\eta_1 M_2}{M_1 \eta_2} \quad (23.4)$$

<sup>1</sup> *Phil. Mag.*, **40**, 421 (1895).

<sup>2</sup> *Verh. deut. physik. Ges.*, **4**, 348 (1902).

<sup>3</sup> K. Schmitt, *Ann. Physik*, **30**, 393 (1909), and previous papers cited there.



which follows from the equation deduced above is either not followed at all or at best only qualitatively.<sup>4</sup>

If gas I is present in large excess over gas II, then

$$\eta = \eta_1 + \frac{c_2}{c_1} \left( \frac{\eta_2}{\beta_2} - \eta_1 \beta_1 \right) \quad (23.5)$$

In this case it can happen that, even if gas II has the smaller viscosity, ( $\eta_2 < \eta_1$ ), the viscosity of the mixture may exceed that of gas I  $\left( \frac{\eta_2}{\beta_2} > \eta_1 \beta_1 \right)$ .

A formula obtained by Pulu<sup>5</sup> by using the average values of the molecular weights, velocities and cross-sections in the simple equation, does not agree well with experiment.

Finally Maxwell<sup>6</sup> has deduced an accurate formula for the case of his special law of force  $K/r^5$ . Enskog gives the exact equation

$$\eta = \frac{\eta_1 \left( 1 + \frac{c_1}{c_2} \beta_2 \right) + \eta_2 \left( 1 + \frac{c_2}{c_1} \beta_1 \right) + A}{\left( 1 + \frac{c_1}{c_2} \beta_2 \right) \left( 1 + \frac{c_2}{c_1} \beta_1 \right) - \frac{A^2}{4\eta_1\eta_2}} \quad (23.6)$$

which differs from Maxwell's expression by the term  $A^2/4\eta_1\eta_2$  in the denominator. For elastic spheres without attractive forces the constants have the values

$$\beta_1 = \frac{1}{12} \left( \frac{d_1 + d_2}{d_1} \right)^2 \sqrt{\frac{2m_2}{m_1 + m_2}} \cdot \frac{5m_1 + 3m_2}{m_1 + m_2} \quad (23.7)$$

$$\beta_2 = \frac{1}{12} \left( \frac{d_1 + d_2}{d_2} \right)^2 \sqrt{\frac{2m_1}{m_1 + m_2}} \cdot \frac{3m_1 + 5m_2}{m_1 + m_2} \quad (23.8)$$

$$A^2 = 16\eta_1\eta_2\beta_1\beta_2 \frac{m_1m_2}{15m_1^2 + 34m_1m_2 + 15m_2^2} \quad (23.9)$$

Trautz and his coworkers<sup>7</sup> have measured the viscosity of a large number of binary gas mixtures. The results are represented by the formula<sup>8</sup>

$$\eta = \eta_1 \left( \frac{Q_1}{Q_m} \right)^2 x^2 + 2\eta_{12} \left( \frac{Q_{12}}{Q_m} \right)^2 x(1-x) + \eta_2 \left( \frac{Q_2}{Q_m} \right)^2 (1-x)^2 \quad (23.10)$$

$$Q_m = Q_1x + Q_2(1-x) \quad (23.11)$$

<sup>4</sup> E. Schröer, *Z. physik. Chem.*, B, 34, 161 (1936) has discussed in detail the behavior of the quantities  $\beta$ , their temperature dependence and the possibility of calculating them from the viscosities of the pure gases. He also compares his results with experiment.

<sup>5</sup> T. Graham, *Phil. Trans. Roy. Soc.*, 136, 622 (1846); J. Pulu<sup>5</sup>, *Wien. Ber.*, 79, 97, 745 (1879); P. Breitenbach, *Wied. Ann.*, 67, 803 (1899); P. Tänzler, *Verh. deut. physik. Ges.*, 8, 222 (1906).

<sup>6</sup> *Phil. Mag.*, 35, 212 (1868); *Scient. Papers*, 2, 72.

<sup>7</sup> M. Trautz *et al.*, *Ann. Physik*, 2 to 22 (1929-1935).

<sup>8</sup> M. Trautz and W. Ludewigs, *ibid.*, 3, 409 (1929).

Here,  $x$  and  $1 - x$  are the mole fractions of the gases, 1 and 2,  $\eta_1$  and  $\eta_2$  their viscosities when pure,  $Q_1$  and  $Q_2$  their scattering cross-sections. The quantities with subscript 12 are due to interactions between molecules of different kinds. The equations contain three adjustable constants,  $Q_1$ ,  $Q_2$ ,  $\eta_{12}Q_{12}^2$ .

Hirschfelder and his coworkers<sup>9</sup> have very successfully calculated the viscosity of binary mixtures and their temperature dependence, according to the methods discussed at the end of Section 21, by using the following constants in the interaction energy (17.9)

$$r_0^{(12)} = \frac{1}{2}(r_0^{(1)} + r_0^{(2)}); \quad \epsilon_{12} = \sqrt{\epsilon_1 \epsilon_2}$$

(24) **Viscosity at Low Density.** (a) **Slippage:** It was found by Kundt and Warburg<sup>1</sup> that, at very low pressures, the apparent viscosity decreases with the pressure (cf. Table V). From this fact they deduced that under these conditions the gas no longer sticks to the moving surface, but slips along it, that is, the layer of gas next to the surface has a velocity of flow different from that of the surface. The relation becomes especially simple if the pressure is so low that practically no collisions between molecules take place in the space between the moving surfaces. This is the case if the mean free path is large in comparison with the distance  $d$  between the surfaces. Then the  $N_A/3V$  molecules per cubic centimeter, which, according to the simplest argument, are considered to have thermal velocities in the vertical direction, simply move back and forth between the plates and are the only ones to hit the plates at all. The  $N_A/6V$  molecules moving downwards have, aside from their thermal velocity  $|\bar{w}|$ , an  $x$ -component of velocity equal to  $W_0$  which they have received upon reflection from the upper plate, while the molecules moving upwards have no excess velocity since they were last reflected from the stationary lower plate. Therefore, the average velocity of the mass motion of the gas does not, as before, increase linearly with  $z$ , but is constant throughout the entire region between the surfaces and equal to  $W_0/2$ , since half the molecules (those moving down) have a velocity of flow  $W_0$  and the other half (those moving up) have zero velocity of flow. At the upper plate there is a discontinuity in velocity equal to

$$W_0 - \frac{W_0}{2} = \frac{W_0}{2} \quad (24.1)$$

and at the bottom plate

$$0 - \frac{W_0}{2} = -\frac{W_0}{2} \quad (24.2)$$

The momentum along the  $x$ -axis received by the lower plate per square centimeter is therefore

$$\frac{M}{6V} |\bar{w}| W_0 = \frac{M |\bar{w}| c}{6} W_0 = \frac{2}{3} \sqrt{\frac{M}{2\pi RT}} p W_0 \quad (24.3)$$

<sup>9</sup> J. O. Hirschfelder, R. B. Bird and E. L. Spotz, *Chem. Rev.*, **44**, 205 (1949).

<sup>1</sup> *Pogg. Ann.*, **155**, 337, 525 (1875); E. Warburg, *ibid.*, **159**, 399 (1876).

since the approaching molecules have a velocity  $W_0$  before reflection and zero velocity afterwards. A more exact calculation<sup>2</sup> shows that the factor  $2/3$  must be replaced by unity. The force is now proportional to the density since the influence of the proportionality of the number of momentum carriers to the density is no longer compensated by a decrease in the distance from which they come, this distance being the constant distance between the plates.

This change of apparent viscosity with pressure has been used to measure very low pressures either by noting the damping of a vibrating quartz fiber<sup>3</sup> or the damping of oscillating plates.<sup>4</sup> Only in the latter case can the absolute viscosity be calculated. Furthermore, Knudsen<sup>5</sup> has used this relation for a determination of the molecular weight of very small amounts of gas. He suspends a glass sphere, 3.4 cm in diameter, from a quartz fiber 18 cm long and  $25.2 \mu$  in diameter. The sphere is surrounded with a closely fitting spherical shell. Torsional oscillations are started in the suspended sphere and the damping (due to the suspension, etc.) is measured in a vacuum. The gas to be investigated is admitted to the space between the sphere and the shell at such a low pressure that the mean free path is large in comparison with the distance from the sphere to the shell and the damping is again determined.

In the general case of moderate pressures it is to be expected that these same conditions as considered above will hold throughout a region adjacent to the moving surfaces and about one mean free path thick, since all the molecules coming up from the lower plate have zero velocity of flow and all those moving downwards have a flow velocity  $W'$  because they come from a layer  $\Lambda$  cm away and  $W'$  is the velocity in that layer. (This is not exact due to the fact that the free paths are not all equal.) This velocity of flow  $W'$  in the next layer is larger, however, than the amount  $\Lambda \partial W / \partial z$  which would at first glance be expected. The reason for this is as follows: In unit time  $\frac{N_A |\bar{w}|}{6V}$  molecules move downward and collide with  $1 \text{ cm}^2$  of the surface.<sup>6</sup>

Each molecule brings to the surface an amount of momentum  $mW'$ . The molecules leaving the surface have, on the average, no excess momentum in the  $x$ -direction. Therefore the amount of momentum brought to unit area of the surface per second is  $\frac{N_A |\bar{w}|}{6V} mW'$  and this must be equal to the flow of

<sup>2</sup> A. Timiriazeff, *Ann. Physik*, **40**, 971 (1913). (Taking into account the change in the distribution of velocity compared with the gas at rest.)

<sup>3</sup> I. Langmuir, *J. Am. Chem. Soc.*, **35**, 107 (1913); F. Haber and F. Kershbaum, *Z. Elektrochem.*, **20**, 296 (1914); A. Coolidge, *J. Am. Chem. Soc.*, **45**, 1637 (1923).

<sup>4</sup> I. Langmuir, *Phys. Rev.*, **1**, 337 (1913); S. Dushman, *ibid.*, **5**, 212 (1915); *Production and Measurement of High Vacuum* (1922); L. Dunoyer, *Vacuum Practice* (trans. by J. H. Smith), (D. Van Nostrand Co., Inc., 1928).

<sup>5</sup> *Ann. Physik*, **44**, 525 (1914).

<sup>6</sup> The more exact calculation of Timiriazeff gives  $3/2$  of this value.

momentum in the interior of the gas; hence,

$$\frac{N_A |\bar{w}|}{6V} m W' = \frac{N_A |\bar{w}|}{3V} \Lambda m \left( \frac{\partial W}{\partial z} \right)_{\text{int}} \quad (24.4)$$

or

$$W' = 2\Lambda \left( \frac{\partial W}{\partial z} \right)_{\text{int}} \quad (24.5)$$

There is, therefore, a more rapid decrease of velocity at the surface. Correspondingly, the velocity at a distance  $\Lambda$  from the upper surface is

$$W_0 - W' = W_0 - 2\Lambda \frac{\partial W}{\partial z} \quad (24.6)$$

The discontinuity in velocity, that is, the difference between the average velocity of the gas at the bottom plate and the velocity of this plate is therefore

$$\frac{1}{2} (W' + 0) = \frac{W'}{2} = \Lambda \frac{\partial W}{\partial z} \quad (24.7)$$

where the first summand corresponds to the molecules coming from above and the second to the reflected molecules. The slope of the velocity gradient within the gas and therewith the force on the plates is decreased by this slip. Within the gas, the velocity decreases from  $W_0 - W'$  (near the upper plate) to  $W'$  over the distance  $d - 2\Lambda$ . Therefore

$$\frac{\partial W}{\partial z} = \frac{W_0 - 2W'}{d - 2\Lambda} = \frac{W_0 - 4\Lambda \frac{\partial W}{\partial z}}{d - 2\Lambda} \quad (24.8)$$

whence <sup>7</sup>

$$\frac{\partial W}{\partial z} = \frac{W_0}{d + 2\Lambda} \quad (24.9)$$

Thus the effect of the slip is equivalent to an increase of the distance between the plates by the amount  $2\Lambda$ . The force then becomes

$$\frac{c |\bar{w}| M \Lambda}{3} \frac{W_0}{d + 2\Lambda} \quad (24.10)$$

instead of

$$\frac{c |\bar{w}| M \Lambda}{3} \frac{W_0}{d} \quad (24.11)$$

(b) **Coefficient of Slip:** These ideas have been generalized still further by Maxwell <sup>8</sup> and also by Knudsen and Smoluchowski through the assumption that a fraction of the molecules hitting the plate equal to  $1 - f$  is reflected

<sup>7</sup> According to Timiriazeff,  $4\Lambda/\pi$  is to be substituted for  $2\Lambda$ . The theory for the numerical factor is quite uncertain.

<sup>8</sup> *Phil. Trans. Roy. Soc.*, 170, 231 (1880).

elastically, the components of velocity in the plane of the plate remaining unchanged. Then only the fraction  $f$  of all the molecules assumes the velocity of the plate ( $W_0$  or 0) upon reflection. These may be thought of as being "emitted" from the plate. Since only this fraction  $f$  transfers momentum to the plates, the equation for  $W'$  takes the form

$$f \frac{c|\bar{w}|}{6} MW' = \frac{c|\bar{w}| \Lambda M}{3} \frac{\partial W}{\partial z} \quad (24.12)$$

Therefore  $W'$ , the velocity of the gas at distance  $\Lambda$  from the bottom plate, is given by

$$W' = 2 \frac{1}{f} \Lambda \frac{\partial W}{\partial z} \quad (24.13)$$

The decrease of velocity within the gas is then

$$\frac{\partial W}{\partial z} = \frac{W_0 - 2W'}{d - 2\Lambda} = \frac{W_0}{d + \frac{2-f}{f} 2\Lambda} \quad (24.14)$$

and the force is

$$F = \frac{c|\bar{w}| M \Lambda}{f} \frac{W_0}{d + \frac{2-f}{f} 2\Lambda} \quad (24.15)$$

The quantity  $\frac{2-f}{f} 2\Lambda$  is called the coefficient of slip. It is inversely proportional to the density and has the dimensions of a length.<sup>9</sup> The change in velocity at the boundary is

$$\frac{1}{2}[W' + (1-f)W' + f.0] = \frac{2-f}{2} W' = \frac{2-f}{f} \Lambda \frac{\partial W}{\partial z} \quad (24.16)$$

Smoluchowski has shown that this same formula is obtained if it be assumed that the velocities of all the molecules after reflection are equal to  $W''$ , which is between the velocity of the plate (0) and the initial molecular velocity ( $W'$ )

$$W'' = (1-f)W' + f.0 \quad (24.17)$$

The physical meaning of  $f$  will be discussed later, and numerical values given (Sections 29 and 30).<sup>10</sup>

<sup>9</sup> The formal hydrodynamic definition of external friction comes from the postulate that the force exerted on the plate by the external friction is equal to the flow of momentum in the interior of the fluid: Coefficient of external friction  $\eta_e \times$  change in velocity at the boundary  $= \eta(\partial W/\partial z)$ .  $\eta/\eta_e$  is defined as the slippage coefficient. From (24.16) it follows that this is in agreement with the present usage. There should appear a numerical coefficient in front of  $\Lambda$  in the denominator. Since attempts at calculating the velocity distribution near the wall have failed, the value of this coefficient is unknown.

<sup>10</sup> Equation (24.4) is valid only if the slip gives only a small correction. For the other extreme, when there are only a few collisions between the plates, see S. Weber, *Physica*, 6, 551 (1939).

(25) The Flow of Gases through Small Orifices at Very Small Pressures: <sup>1</sup>

Gas flow through orifices is also a case in which the behavior at very low pressures is quite different from that at normal pressures. The case of low pressures will be treated first because it is simpler.

Consider a vessel connected to an evacuated space through a small opening in a thin wall. Throughout this discussion a pressure will be considered low if the mean free path of the gas at that pressure is large in comparison with the dimensions of the orifice. Similarly a high pressure is one at which the mean free path is small in comparison with the dimensions of the orifice.

If the orifice is small in comparison with the mean free path, a molecule upon hitting the opening will not, in general, collide with another molecule in the orifice but will continue to move in the direction of its original velocity. On the other hand, the distribution of the gas molecules inside the vessel in the neighborhood of the small hole is only slightly different from that prevailing at any other point near the wall. Consider, for example, that the opening is closed for an instant. Most of the molecules which move chaotically at a distance  $\Lambda$  (one free path) from the closed orifice come from the interior of the gas or have just been reflected from that part of the wall which does not constitute the opening.<sup>2</sup> The fraction of these molecules which have been reflected from the covering of the hole, and which will be missing upon removal of the covering, is very small ( $\sim$  area of hole/ $4\pi\Lambda^2$ ). At the distance  $\Lambda$  from the opening, therefore, the presence of the opening does not greatly affect the distribution of the gas. Since, however, the molecules hitting the hole come from a distance  $\Lambda$  (if, as has been assumed, the opening in question is in a large plane wall) their number can be set equal to the number of molecules hitting an area of the original unperforated wall equal to the area of the opening,  $A$ . This number is equal to

$$\begin{aligned} N &= \frac{1}{4} AN_A c |\bar{w}| \\ &= \frac{1}{4} AN_A c 2 \sqrt{\frac{2kT}{\pi m}} = \frac{AN_A p}{\sqrt{2\pi MRT}} \end{aligned} \quad (25.1)$$

Thus, the amount of gas flowing out through the orifice is proportional to the area of the orifice, to the density, to the square root of the temperature and inversely proportional to the square root of the molecular weight. In a mixture of several gases each constituent flows through the opening as if the others were not present.

The molecules move into the evacuated space with velocities of the same magnitude and direction that they had upon passing through the orifice, that is to say, their velocities are distributed uniformly in all directions. The open-

<sup>1</sup> Clerk Maxwell, *Phil. Trans. Roy. Soc.*, **170**, 231 (1880); *Scient. Papers*, **2**, 681, 711 (Cambridge, 1890).

<sup>2</sup> K. Bennowitz, *Z. physik. Chem.*, **B**, **49**, 293 (1941) has calculated the "tarrying distance" inside the vessel as  $4v/\Lambda$ .

ing acts as if the molecules left it in the same manner in which light leaves a glowing surface (Lambert's cosine law).<sup>3</sup> There is, therefore, no formation of a ray. If the region outside the containing vessel were not completely evacuated but contained a rarefied gas, which might or might not be the same as the first, the amount of gas passing through the opening from the inside would not be affected by this fact and is therefore again given by Equation (25.1). Since negligibly few collisions take place within the orifice a similar statement holds for the flow of gas in the reverse direction. Consider, for example, the case in which oxygen is the gas within the vessel and hydrogen at an equal pressure is outside. At the start of the flow, the pressure within the vessel increases because hydrogen, due to its sixteen times smaller molecular weight, comes in four times as fast as the oxygen leaves. On the other hand, the partial pressure of the oxygen is continually decreasing on the inside and increasing on the outside until equality is reached. Similarly, the partial pressure of the hydrogen on the inside increases and on the outside decreases until it also is equalized. Even if the initial pressure of the oxygen is twice as great as that of the hydrogen, a larger amount of hydrogen will flow in at the beginning so that the pressure difference increases. Of course work obtained from this process would not be in contradiction to the second law of thermodynamics, since the pressure increase is merely due to the free energy decrease attending the irreversible expansion upon diffusion. Analogies to this will appear in other phenomena of flow through capillary tubes which, together with their applications, will be discussed below.

The relations deduced in this section have been employed by a number of investigators for various physical measurements. Knudsen<sup>4</sup> has shown that Equation (25.1) can be used to determine either the molecular weight of the flowing gas or its temperature. He has also applied the relation to the measurement of the vapor pressure of mercury. Other workers<sup>5</sup> have utilized the same general method to determine various other small vapor pressures. The experiment consists merely in determining the weight of material flowing in unit time at constant temperature through a small hole of known area. Since all the other quantities in Equation (25.1) are known, the vapor pressure follows from a simple calculation.

Weide and Bichowsky<sup>6</sup> have developed a method for the determination of the degree of dissociation of a gas at various temperatures by studying the effusion of the gas through a small hole. In their experiment, a small constant flow of the gas to be studied is established through the apparatus. The gas is led at a pressure of a few tenths of a millimeter of mercury to a furnace from which it escapes through a small hole to a highly evacuated space. The high

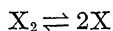
<sup>3</sup> H. Mayer (*Z. Physik*, **52**, 235 [1928]) has given an experimental proof of this statement. He measured by means of a torsion balance the number of molecules leaving a small hole.

<sup>4</sup> *Ann. Physik*, **28**, 998 (1909); **29**, 179 (1909).

<sup>5</sup> A. C. Egerton, *Phil. Mag.*, **33**, 33 (1917); *Proc. Roy. Soc., A*, **130**, 469 (1923); T. H. Swan and E. Mack, Jr., *J. Am. Chem. Soc.*, **47**, 2112 (1925).

<sup>6</sup> *Ibid.*, **48**, 2529 (1926).

pressure side of the small hole is connected to an accurate pressure measuring device. If the temperature of the furnace is raised, the gas in front of the small hole is partially dissociated according to the reaction



The pressure on the high pressure side of the small hole will have to be changed since the number of molecules passing through the small hole in unit time has to be increased in order to keep the total mass flowing unchanged. Thus, if there were no dissociation, the pressure would be  $p'$  given by the equation

$$N' = \frac{AN_A p'}{\sqrt{2\pi M_{X_2} RT}} \quad (25.2)$$

where  $N'$  is the number of molecules ( $\text{X}_2$ ) entering the apparatus in unit time. If, however, the gas is dissociated, the atomic and molecular forms do not interfere with each other as to flow, so that

$$N_{X_2} = \frac{AN_A p_{X_2}}{\sqrt{2\pi M_{X_2} RT}} \quad (25.3)$$

and

$$N_X = \frac{AN_A p_X}{\sqrt{2\pi M_X RT}} \quad (25.4)$$

where  $N_{X_2}$  is the number of molecules flowing out per second and  $N_X$  the number of atoms,  $p_{X_2}$  and  $p_X$  being the respective partial pressures. Since

$$N' = N_{X_2} + \frac{1}{2}N_X$$

and

$$p = p_{X_2} + p_X$$

where  $p$  is the measured total pressure at the small hole, there may be obtained the relation

$$p_X = \frac{\sqrt{2}}{\sqrt{2} - 1} (p - p') \quad (25.5)$$

Since  $p$  is measured directly and  $p'$  may be calculated, the partial pressure of the atomic form follows at once. De Vries and Rodebush<sup>7</sup> have used this method to determine the equilibrium constants for the dissociation of iodine and bromine. It has also been used by Bichowsky and Copeland<sup>8</sup> for the determination of the degree of dissociation of the hydrogen drawn from a discharge tube. This latter quantity has also been measured by Wrede.<sup>9</sup> Instead of measuring a steady flow, he investigated the pressure difference across a small hole through which there is no resulting transport of mass. A glass wall perforated by a small orifice separates two vessels, both of which are

<sup>7</sup> *Ibid.*, 49, 656 (1927).

<sup>8</sup> *Ibid.*, 50, 1315 (1928).

<sup>9</sup> *Z. Instrumentenk.*, 48, 201 (1928); *Z. Physik*, 54, 53 (1929).



closed. In one of them the dissociation process takes place, Wrede using for this purpose an electric discharge rather than heat. The other vessel contains a catalyst placed before the orifice so that particles entering through the opening strike the catalyst immediately, atoms combining to form molecules. The resulting formula is again (25.5).

*Molecular Rays:* A further application of the flow through small orifices has been found in the production of rays of molecules. Modern vacuum pumps have permitted experiments with molecular rays, i.e., streams of molecules flying almost parallel to each other.<sup>10</sup> If these rays are to persist practically undisturbed over about 10 cm, for example, the density of the surrounding gas must be so low that the mean free path is larger than 10 cm; this means the pressure must be below  $3 \times 10^{-4}$  mm Hg. The sources of the rays may be of two kinds, depending on the gas. If it is a permanent gas, muzzles are used; if it is a vapor, a small oven electrically heated is employed. The pressure in the oven or muzzle is higher than in the surrounding gas (perhaps 0.01 mm), the orifice being smaller than the mean free path corresponding to the pressure inside. As the gas molecules coming from the opening have directions spread over a half sphere (less in a properly designed muzzle) a series of diaphragms are needed to constrict the beam. The molecules not passing the diaphragms are either frozen out on hitting the surface or pumped out, which necessitates a subdivision of the vessel into an oven part and an observation part.

The type of receiver depends also on the nature of the gas. With metal vapors, like silver, the molecular rays are allowed to condense on a glass or brass plate. For alkali metal vapors, a method developed by Taylor and Langmuir<sup>11</sup> can be used. Potassium atoms striking a tungsten surface lose their electrons to the tungsten, and if the metal is at about 1400°C, the striking atoms leave the surface again as ions. It is therefore only necessary to measure the negative current to find the number of atoms striking. For sodium, which has a higher electron affinity, the tungsten surface must first be covered with a film of oxygen.

For permanent gases a manometer has been developed by Stern and by Zabel.<sup>12</sup> It consists of a small metal vessel with an opening, placed in front of the beam. A pressure is built up inside until in the stationary state the number of beam molecules  $Z$  falling per second on the opening  $A$  is equal to the number leaving the manometer in all directions according to (25.1),

$$Z = \frac{AN_A}{\sqrt{2\pi MRT}} p \quad (25.6)$$

<sup>10</sup> R. G. T. Fraser, *Molecular Rays*, (New York: The Macmillan Co., 1931); W. H. Rhodembush, *Rev. Mod. Phys.*, 3, 392 (1931); V. Guillemin, Jr., *J. Franklin Inst.*, 219, 73 (1935); K. F. Herzfeld in *Hand- und Jahrb. Chem. Physik*, Vol. 3, Sec. 2, IV, Leipzig: Akademische Verlags Ges. (1939).

<sup>11</sup> I. Langmuir and K. H. Kingdon, *Proc. Roy. Soc.*, A, 107, 601 (1925); J. B. Taylor, *J. Physik*, 57, 242 (1929).

<sup>12</sup> F. Knauer and O. Stern, *Z. Physik*, 53, 766 (1929); T. H. Johnson, *Phys. Rev.*, 31, 103 (1928); A. Ellett and R. M. Zabel, *ibid.*, 37, 1102, 1112 (1931).

The pressure  $p$  is measured with the help of a thin heated wire within the manometer which is used at the same time as a resistance thermometer and so measures the pressure in the manometer through the heat conduction which is proportional to  $p$  (see Section 32).

The sensitivity can be increased by measuring, instead of the heat conduction, the ionization produced in the gas by electrons emerging from a hot wire cathode.

(26) **Flow at Average and Higher Pressures:** If the dimensions of the orifice are large in comparison to the mean free path, the situation is quite different. The disturbance caused by the presence of the orifice is evident throughout the gas near the opening. The distribution of velocity within the vessel is changed so that there is a motion of the entire gas in the neighborhood toward the opening. The kinetic energy of the discharged gas is no longer distributed symmetrically between the three coordinate directions but there is a kinetic energy of the gas as a whole and hence a pronounced jet of gas leaves the orifice. Here the flow is determined by the total pressure difference across the orifice. Thus, to return to the previous illustration, if the oxygen pressure inside the vessel equals the hydrogen pressure outside, there is, on the whole, no flow of gas, because there is no difference in the *total* pressure on the two sides of the orifice. The partial pressures are equalized by diffusion (Section 42). If the oxygen pressure inside is greater than the hydrogen pressure outside, the oxygen flows out on account of the difference in total pressures, and the inward diffusion of the hydrogen does not begin until the total pressures have become equal or at least nearly so. (For the effect of temperature differences, cf. (Section 44).

Further problems arising in this connection have not been investigated from the point of view of the kinetic theory of gases (e.g., with regard to the distribution of velocities). Rather must they be attacked with the methods of hydrodynamics. The theory of gases has been applied only in so far as it is capable of leading to the deduction of the hydrodynamic or aerodynamic equations, including their supplementary terms (see Section 16).

Bunsen<sup>1</sup> has determined the molecular weights of gases by allowing the gas to stream out of a hole 0.1 to 0.01 mm diameter and setting the volume passed in unit time proportional to  $1/\sqrt{M}$ . This procedure, however, is not founded on the kinetic theory directly, but on hydrodynamics, since it determines primarily the density of the gas. The kinetic energy of the flow is determined principally by the pressure difference; it also depends on  $C_p/C_v$  and must be corrected for friction. The pressure difference being kept the same, the kinetic energy  $\frac{1}{2}\rho v^2$  will be the same and therefore the velocity inversely proportional to the square root of the density. But, from the gas laws, the density is proportional to  $M$ , hence the volume passed in unit time is inversely proportional to the square root of the molecular weight.

<sup>1</sup> *Gasometrische Methoden*, (Brunswick: 1857). Cf. also H. Eyring, *J. Am. Chem. Soc.*, 50, 2398 (1928).

Further information regarding the carrying out of these measurements and the results obtained from them may be found in the standard texts on hydrodynamics.

(27) **Flow through Tubes:** Consider now the case in which the two vessels are connected by means of a tube instead of an orifice. The tube is to be straight and of circular cross-section with diameter  $d$ .

(a) *Mean Free Path Large in Comparison to  $d$ :* The flow of gas under this condition has been named by Knudsen "molecular flow."<sup>1</sup> If the gas molecules were reflected elastically from the wall of the tube (which is supposed smooth), the flow through the tube would be identical with the previously discussed case of the flow through an orifice in a plane, thin wall. All the molecules entering the mouth of the tube would pass through into the second vessel. That is, the quantity of gas flowing through the tube in unit time would be independent of the length of the tube and equal to the amount of gas passed by an orifice of equal size under the same conditions of pressure, etc. Moreover, the directions of the velocities of the molecules would be distributed as in the previous case. Since, however, the amount of gas passed is found to depend on the length of the tube, the assumption of elastic reflections from the tube wall cannot be correct. To take the place of this assumption, Knudsen has postulated that "emission" takes place from the wall of the tube instead of reflection. By this it is meant that the molecules leave a surface uniformly in all directions regardless of the directional distribution with which they hit the surface.<sup>2</sup> As a result of this behavior, some entering molecules are sent back to the vessel from which they came. The longer the tube, the greater the fraction of molecules thus returned. Hence the amount of gas flowing through the tube must diminish with increasing length of the tube. According to this hypothesis, the number of molecules entering the tube which are turned back within it, returning to the vessel from which they came, is a certain fraction of the total number of entering molecules. This fraction is determined only by the number of collisions with the wall of the tube and not by collisions between molecules. It is therefore independent of the concentration of the gas, the molecular diameter and the presence of another gas (provided that the mean free path of the other gas is also large in comparison with the diameter of the tube.)

If  $Z$  is the number of molecules hitting unit area in unit time, the excess flow of molecules from left to right (along the positive  $x$ -axis) is found to be<sup>3</sup>

$$\frac{1}{2} B \frac{dZ}{dx} \quad (27.1)$$

<sup>1</sup> *Ann. Physik*, **28**, 75 (1909); **35**, 389 (1911); M. von Smoluchowski, *ibid.*, **33**, 1559 (1910). Cf. also O. Reynolds, *Phil. Trans. Roy. Soc.*, **170**, 727 (1880); *Papers*, I, 257, Cambridge (1900).

<sup>2</sup> See discussion by P. Clausius, *Ann. Physik*, **4**, 533 (1930); **7**, 569 (1930).

<sup>3</sup> The deduction is as follows. The number of molecules hitting a certain part of the wall will first be investigated in respect to the point from which they come. An elemen

where for circular tubes

$$B = 2d^3\pi \quad (27.2)$$

Since the quantity  $Z$  decreases linearly with  $x$ , and since its value at the inlet to the tube is

$$N_A c_2 |\bar{w}_2| = N_A \frac{p_2}{\sqrt{2\pi MRT_2}} \quad (27.6)$$

$dA'$  of the tube wall sends out a cone of molecules (Fig. 23). The solid angle of the cone is  $d\omega' = \sin \varphi' d\varphi' d\epsilon'$  where  $\varphi'$  is the angle between the axis of the cone and the normal to the surface and  $\epsilon'$  an angle measured in the plane of  $dA'$  from an arbitrary line in this plane, corresponding to the geographical longitude. ( $\varphi'$  and  $\epsilon'$  are the angles of a set of space polar coordinates with axis normal to  $dA'$ .) The number of molecules sent out into this cone from the element  $dA'$  in unit time is

$$Z' \frac{d\omega'}{\pi} \cos \varphi' dA' \quad (27.3)$$

because the quantity  $\cos \varphi' dA'$  is the projection of the surface  $dA'$  on a plane perpendicular to the axis of the cone (the name Cosine Law being due to the factor  $\cos \varphi'$ ). This solid angle  $d\omega'$  is completely filled by another elementary surface  $dA$  at a distance  $r$  from  $dA'$  if

$$d\omega' = \frac{dA \cos \varphi}{r^2} \quad (27.4)$$

where  $\varphi$  is the angle between the normal to  $dA$  and the axis of the cone. (The numerator of this expression is, as before, the projection of  $dA$  perpendicular to the axis of the cone.) The number of molecules crossing the surface  $dA$  and coming from the direction of  $dA'$  is then

$$\frac{Z' \cos \varphi' \cos \varphi}{\pi r^2} dA dA'$$

But the total number of molecules crossing this surface  $dA$  coming from all possible directions (from all the elements of area  $dA'$ ) is

$$\begin{aligned} \frac{dA}{\pi} \int \frac{Z' \cos \varphi \cos \varphi'}{r^2} dA' \\ \frac{dA}{\pi} \int Z' \cos \varphi \sin \varphi d\varphi d\epsilon \\ d\omega = \sin \varphi d\varphi d\epsilon : \frac{dA' \cos \varphi'}{r^2} \end{aligned} \quad (27.5)$$

is the solid angle which originates at  $dA$  and is subtended by  $dA'$ .

The dependence of  $Z$  on  $x$  can be found from the consideration that the number of molecules leaving a portion of the wall must be equal to the number coming to that portion from elsewhere. It is found that  $Z$  varies linearly along the tube. The details of the calculation can be found in the 2d ed. of this treatise, p. 171.

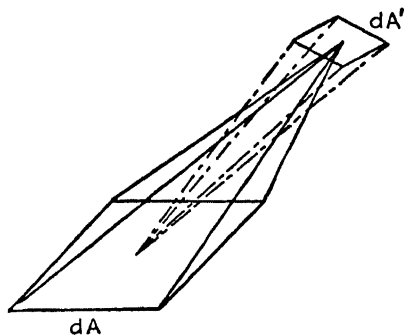


FIG. 23.

and at the outlet is

$$\frac{N_A c_1 |\bar{w}_1|}{4} = N_A \frac{p_1}{\sqrt{2\pi MRT_1}} \quad (27.7)$$

the number of mols of gas flowing through the tube per second is given by

$$\frac{dn}{dt} = \frac{1}{2} B \frac{1}{\sqrt{2\pi MR}} \left( \frac{p_2}{\sqrt{T_2}} - \frac{p_1}{\sqrt{T_1}} \right) \frac{1}{L} \quad (27.8)$$

where  $L$  is the length of the tube.

For the case of constant temperature this becomes

$$\frac{dn}{dt} = \frac{1}{2} \frac{B}{\sqrt{2\pi MRT}} \frac{1}{L} (p_2 - p_1) = \frac{1}{2} \frac{B}{\sqrt{2\pi M}} \frac{\sqrt{RT}}{L} (c_2 - c_1) \quad (27.9)$$

This equation is formally the same as the one obtained for small orifices

$A \sqrt{\frac{RT}{2\pi M}} (c_2 - c_1)$  with the exception that in the place of  $A$  there appears the quantity

$$\frac{B}{2L} = \text{cross section} \frac{4d}{3L}$$

(for cylindrical tubes).

In the case of non-cylindrical tubes, provided that the dimensions are so small that there are only collisions with the wall and negligibly few between molecules, there is to be expected a formula of the type

$$B' : (p_2 - p_1) \quad (27.10)$$

where  $B'$  has the dimensions of an area and depends only on the dimensions and shape of the tube and not on the gas.<sup>4</sup>

If there exists an accommodation coefficient  $f < 1$ , instead of the case where all molecules are emitted, the right side of (27.8) is to be multiplied\* by

<sup>4</sup> For a cylindrical tube we introduce the plane polar coordinates  $r, \vartheta$  in a cross-section of the tube and find, for the flow through that cross-section:

$$\frac{1}{2} \frac{dZ}{dx} dA \frac{d}{2} \int_0^{2\pi} \frac{\frac{r}{2} + r \cos \vartheta}{\sqrt{\frac{d^2}{4} + r^2 + rd \cos \vartheta}} d\vartheta \quad (27.11)$$

The greatest flow prevails at the center ( $r = 0$ ). Upon integrating over  $dA = 2\pi r dr$  there is obtained the value of  $B$  given above. For square cross sections this quantity is 2.973  $l^2$ . For rectangles, see Smoluchowski (*loc. cit.*).

\* If only the fraction  $f$  of the molecules colliding with the wall is emitted, the remainder,  $1 - f$ , being reflected, the  $Zf$  emitted molecules introduce the factor  $f$  into Equation (27.10). The  $1 - f$  molecules coming from the left which were reflected at the point  $x_0 + (x' - x_0)$

$(2 - f)/f$ . This correction <sup>5</sup> is valid only as long as  $f$  is sufficiently large or the tube sufficiently long to ensure that each molecule is emitted repeatedly from the wall. The case of shorter tubes has been treated by Clausius.<sup>6</sup>

In all these cases, the amount of gas flowing per unit time will be directly proportional to the pressure difference, inversely proportional to the square root of the temperature (or directly proportional to the difference in concentration and the square root of the temperature) and inversely proportional to the square root of the molecular weight. Graham <sup>7</sup> discovered these results long before the development of the kinetic theory in the course of his experiments upon the passage of gases through porous plates such as gypsum and meerschaum, the pores of such materials being small in comparison to the mean free path. His results have been checked by other workers.

The point must be emphasized here that in the motion of a mixture of gases, each constituent is completely independent of the others, as is the case with small orifices, since the molecules do not affect each other within the tube and since their motion is entirely determined by the character of the wall of the tube, the temperature and molecular weight of the gas molecules.

The dependence of the velocity of effusion upon molecular weight has been used to detect fire damp in mines. For this purpose a closed porous vessel (e.g., gypsum) filled with air is attached to a pressure measuring device which can actuate an alarm. If fire damp ( $\text{CH}_4$ ,  $M = 16$ ) is present in the external

have come there from the point  $x_0 + 2(x' - x_0)$  (Fig. 24). Of these molecules the fraction  $f$  had been emitted from the point  $x_0 + 2(x' - x_0)$  and the reflected fraction,  $1 - f$ , had come from a point still farther to the left. The  $f(1 - f)Z(x_0)$  molecules which are emitted at the point  $x_0 + 2(x' - x_0)$  and which are then reflected unchanged from the point  $x_0 + (x' - x_0)$  add to the flow twice as much as would the same number of molecules emitted at the point  $x'$  because they come twice as far. Furthermore, there are missing from the molecules which pass the point  $x_0$  to the left, coming from the right, those which have not been emitted to the left at the point  $x_0 - (x' - x_0)$  but which were reflected to the right at this point. This portion,  $f(1 - f)B(dZ/dx)dA$ , which is missing from the reverse current, also increases the excess flow to the right so that those molecules which are reflected once contribute to the flow an amount equal to  $3f(1 - f)(dZ/dx)B$ . Correspondingly, the contribution from those which are reflected twice in succession is equal to  $(3 + 2)f(1 - f)^2(dZ/dx)B$ . On summing, the factor to be applied to (27.15) is

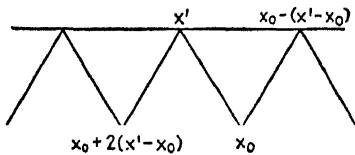


FIG. 24.

$$f[1 + 3(1 - f) + 5(1 - f)^2 + \dots] = \frac{2 - f}{f} \quad (27.12)$$

<sup>5</sup> For a discussion of the bearing of flow experiments on our knowledge of  $f$ , see P. Clausius, *Ann. Physik*, **4**, 567 (1930).

<sup>6</sup> *Idem*, *ibid.*, **12**, 961 (1932).

<sup>7</sup> *Quart. Journ. of Science*, **2**, 74 (1829); *Phil. Mag.*, **2**, 175, 269, 351 (1833); *Pogg. Ann.*, **17**, 341 (1829); **28**, 331 (1833); **120**, 415 (1863); *Phil. Trans. Roy. Soc.*, 385 (1863); G. Hüfner, *Wied. Ann.*, **16**, 260 (1882); E. Reusch, *Pogg. Ann.*, **124**, 434 (1865). Bunsen's anomalous results, according to Graham, are to be attributed to too large openings (R. Bunsen, *Gasometrische Methoden*, Brunswick, 1857).

air ( $M \sim 29$ ) the pressure within the porous container increases and causes the alarm to sound. The velocity of effusion may also be used for the determination of molecular weight of gases (atmolysis). Conversely, mixtures of gases of different molecular weights can be fractionally separated by effusion.<sup>8</sup> It is possible to keep the pressure on the output side low with the help of a vapor blowing rapidly past the porous layer; the vapor is then removed by condensation. The method has been applied to the separation of isotopes.<sup>9</sup> If the holes are larger than a mean free path, there is also a mass flow which does not contribute to the separation.<sup>10</sup> However, even for large holes separation is possible with the help of the flowing vapor.<sup>11</sup>

To return again to the case of the small tube of circular cross-section some numerical examples will be given. It must be remembered that the mean free path in hydrogen at a pressure of 0.1 mm Hg equals about 1 mm. Suppose a space, in which a constant pressure of hydrogen equal to 0.1 mm is maintained, be connected through a tube 1 mm in diameter and 5 cm long to a completely evacuated chamber. According to Equation (27.8), 40 cm<sup>3</sup> of the gas at 0.1 mm ( $24 \times 10^{-8}$  mole) flow through the tube per second, a quantity which can be removed by good pumps. This is of fundamental importance in the investigation of molecular rays or ion beams which can only be produced in a space filled with gas, but which must be studied either in a high vacuum or in a different gas. M. Knudsen has investigated the flow through still smaller tubes. For example, he connected two flasks of 2½ liters contents by means of a tube 30 cm long and 0.1 mm in diameter. One flask was filled with hydrogen at about 0.01 mm and the other was evacuated to as low a pressure as possible. It required about fifteen hours for one third of the gas to pass from the one flask to the other. The agreement with the formula (27.9) is satisfactory. Furthermore, according to (27.9) the time is independent of the total pressure if the latter is sufficiently small.

(b) *Poiseuille Flow*: This type of flow takes place through tubes whose diameters are large in comparison with the mean free path, but which are still small enough to be regarded as capillary tubes, which means that the viscosity is still an important factor. For small rates of flow the motion is determined by Poiseuille's law, which states that the volume of fluid passing through the tube in unit time is

$$\frac{d^4\pi}{128} \frac{p_2 - p_1}{\eta L} \quad (27.13)$$

<sup>8</sup> F. Fischer, H. Schrader, and A. Jager, *Brennstoff-Chem.*, **4**, 289 (1923); R. Lorenz and A. Magnus, *Z. anorg. Chem.*, **136**, 97 (1924).

<sup>9</sup> G. Hertz, *Physik. Z.*, **23**, 433 (1922); *Z. Physik*, **19**, 35 (1923); R. S. Mulliken and W. I. D. Harkins, *J. Am. Chem. Soc.*, **44**, 37 (1922); D. E. Wooldridge and W. R. Smythe, *Phys. Rev.*, **50**, 233 (1936); H. de W. Smyth, *Atomic Energy for Military Purposes* (Princeton, N. J.: Princeton University Press, 1945).

<sup>10</sup> K. Kammermeyer and H. T. Ward, *Ind. Eng. Chem.*, **33**, 474 (1941); E. Wicke and R. Kallenbach, *Z. f. Kolloid*, **97**, 131 (1941).

<sup>11</sup> C. G. Maier, *J. Chem. Phys.*, **7**, 854 (1939); *Bull. U. S. Bur. of Mines*, No. 431, 1940; F. A. Schwertz, *Phys. Rev.*, **68**, 145 (1945).

where  $L$  is the length of the tube. The deduction of this equation may be found in any standard text on hydrodynamics.<sup>12</sup>

The equation giving the flow in moles per second may also be written

$$\frac{d^2\pi}{12} \frac{3d^2}{32\Lambda} \left| \bar{w} \right| \frac{\partial c}{\partial x} \quad (27.14)$$

If there were present no unsymmetrical velocity of flow (no deviation from Maxwell's law) a deduction of the type employed in Section 21 would give the equation

$$\frac{d^2\pi}{12} \left| w \right| \Lambda \frac{\partial c}{\partial x} \quad (27.15)$$

Actually, however, the flow is greater by the amount  $3d^2/32\Lambda^2$ .

The main difficulty encountered in applying this equation to the flow of gases is that it is valid as it stands for an incompressible fluid but, in the case of a gas, the specific volume changes along the tube with the pressure. Furthermore, a change in temperature is in general connected with the change in volume and the extent of this temperature change depends on the circumstances (properties of the tube wall). Under different conditions the expansion may be isothermal or adiabatic.

For a short interval of the tube the flow in moles may be written

$$\frac{dn}{dt} = \frac{d^4\pi}{128L} \int \frac{1}{\eta RT} p dp \quad (27.16)$$

For an isothermal process with the limitation that  $\eta$  is constant,<sup>13</sup> this gives the expression

$$\frac{dn}{dt} = \frac{d^4\pi}{128L\eta} \frac{1}{RT} \frac{p_2^2 - p_1^2}{2} \quad (27.17)$$

The case of a polytropic expansion, i.e., one intermediate between an isothermal and adiabatic, has been treated by Fisher and by Holm,<sup>14</sup> but the measurement of Trautz and Weizel<sup>15</sup> and of Benton<sup>16</sup> are represented better by the isothermal equation.

The rate of flow can be used as a means of determining  $\eta$ .

The most precise application of this method is due to Bond.<sup>17</sup>

Two further corrections, however, must be applied to the formula before it can be used. It must be pointed out first that only part of the pressure difference is utilized in overcoming friction, the remainder being required for the

<sup>12</sup> See M. Brillouin, *Leçons sur la viscosité*, Paris, 1907; also, *Hydrodynamics*, Bull. No. 84 (Washington, D. C.: Natl. Res. Council, 1932).

<sup>13</sup> O. E. Meyer, *Pogg. Ann.*, 127, 253, 353 (1866).

<sup>14</sup> J. Fisher, *Phys. Rev.*, 29, 149 (1909); R. Holm, *Ann. Physik*, 44, 81 (1914); 45, 1165 (1914).

<sup>15</sup> *Ibid.*, 78, 305 (1925).

<sup>16</sup> *Phys. Rev.*, 14, 403 (1919).

<sup>17</sup> *Proc. Phys. Soc.*, 49, 205 (1937).



production of the kinetic energy of the mass motion. This latter portion, which was first considered by Hagenbach<sup>18</sup> and later by Brillouin (*loc. cit.*) and Smoluchowski<sup>19</sup> must be subtracted from the pressure difference. (Cf. Equation [27.18].)

In the second place the gas does not stick to the walls of the tube, as has already been noted on p. 91 in Section 24 and as was first demonstrated experimentally by Warburg.<sup>20</sup> A finite slip with slippage coefficient  $\frac{\eta}{\eta_e}$ , where

$\frac{\eta}{\eta_e} \cdot \frac{\partial W}{\partial r}$  = discontinuity in velocity at the boundary of the flowing gas,  $\frac{\eta}{\eta_e} = \frac{2-f}{f} \Lambda$  (see Equation [24.15]), requires the insertion of the factor  $\left(1 + \frac{8\eta}{\eta_e d}\right)$  in Equation (27.15). It has already been shown that  $\eta/\eta_e$  is directly proportional to the mean free path and is therefore inversely proportional to the pressure. The formula giving the number of moles flowing per second is then<sup>21</sup>

$$\frac{dn}{dt} = \frac{1}{8\eta L} \left(1 + \frac{8\eta}{\eta_e d}\right) \left[ \frac{\pi d^4}{16RT} \frac{(p_2^2 - p_1^2)}{2} - \frac{M}{\pi} \left(\frac{dn}{dt}\right)^2 \right] \quad (27.18)$$

where the last term, which takes into account the kinetic energy, is only a correction term.

The discussion of (27.18) leads to the following conclusions. If the pressure difference is held constant and the correction for kinetic energy neglected, the quantity of gas flowing decreases with decrease in pressure. Hence the amount of moles passed per second is proportional to  $\frac{\alpha}{\Lambda} + \beta$ . However, as soon as the motion is no longer determined by collisions between molecules but by collisions with the wall the quantity of gas passing is independent of the pressure. If the flow of gas is expressed in terms of the volume or fractions of the amount of gas present in a vessel, the flow *increases* with decrease in pressure up to a certain value, after which it remains constant. The fact that upon evacuating a system the volumes removed decreases as the pressure falls, is explained by continuous decrease in the *pressure difference* upon which the flow depends. At very small pressures the term  $8\eta/\eta_e d$ , corresponding to the slip, predominates and the equation reduces to (27.8) with, however, a different numerical factor. Using (21.9), (21.10) and (24.5) we end up with formula (27.9) and the  $B$  value (27.2), multiplied by  $(2-f)/f$  according to (27.12). There is a numerical factor  $3\pi/0.499 \times 32 = 0.588 = 1/1.7$ . This can be corrected formally, without theoretical explanation, by multiplying  $8\eta/\eta_e d$  in (27.18) by

<sup>18</sup> *Pogg. Ann.*, **109**, 835 (1860).

<sup>19</sup> *Bull. Acad. Krakau*, **143** (1903).

<sup>20</sup> *Pogg. Ann.*, **59**, 399 (1876).

<sup>21</sup> Maxwell obtained this formula, except for the term correcting for the kinetic energy, from the theory of gases (*loc. cit.*, p. 709). Reynolds (*loc. cit.*, p. 351) has also arrived at an expression of similar character.

$1.7(1 + Cp)(1 + 1.7Cp)^{-1}$ , where  $C$  is a constant. For large  $p$ , this reduces to unity, for small  $p$  it reduces to 1.7.

Knudsen, using different numerical factors in (21.9) and (21.10), has obtained an equivalent expression of different form and with different numerical values, namely

$$\frac{dn}{dt} \bigg/ \frac{p_2 - p_1}{L} = \frac{\pi d^4}{128\eta RT} \cdot \frac{p_2 + p_1}{2} + \frac{\pi d^3}{3} \cdot \frac{1}{\sqrt{2\pi RTM}} \cdot \frac{1 + c_1 p}{1 + c_2 p} \quad (27.19)$$

$c_1 = 2.00$ ,  $c_2 = 2.43$ , if  $p$  is measured in dynes per square centimeter. Knudsen's formula fits his experiments for the flow of hydrogen, oxygen, and carbon dioxide in the pressure interval of 15 mm Hg down to  $10^{-4}$  mm. At low pressures, there occurs, in accordance with the formula, a minimum of flow, when the mean free path is about five times the radius of the capillary. The flow there is 95 percent of that at the very low pressures.<sup>22</sup> For a slit, Clausius<sup>23</sup> shows that if  $L > a > b$ ,

$$B = ab^2 \left( \frac{1}{2} + \ln \frac{2a}{b} \right) \quad (27.20)$$

in accordance with Smoluchowski. If  $a > L > b$ ,

$$B = ab^2 \left( \frac{1}{2} + \ln \frac{L}{b} \right) \quad (27.21)$$

Here  $a$  is the length of the slit,  $b$  its width and  $L$  its depth.

Gaede<sup>24</sup> has tested the flow through slits at low pressures and found also a minimum. Clausius has shown that if the correct theoretical formula is used, the agreement is good. Rasmussen<sup>25</sup> also confirmed Clausius's results.

(c) *Other Shapes*: The flow between two plates a small distance  $d$  apart is given by the expression

$$\text{Moles passing 1 cm width per second} = \frac{d^3}{12\eta RT} \frac{1}{2} \frac{p_2^2 - p_1^2}{2} \quad (27.22)$$

Reynolds has deduced a similar formula from the theory of gases. If the plates are very close together,  $d$  being of the order of  $10^{-4}$  cm, the amount of air at atmospheric pressure flowing through a width of 1 cm under a pressure gradient of 1 mm Hg/cm equals  $0.6 \times 10^{-6}$  cm<sup>3</sup>/sec. Stefan<sup>26</sup> has concluded from this that the difficulty attending the separation of two smooth plates which are in close contact, depends less upon the presence of attractive forces (adhesion) than upon the slow entry of the air through the narrow slit. The

<sup>22</sup> W. Klose, *Ann. Physik*, 11, 73 (1931); *Physik. Z.*, 31, 503 (1930). The author found that bends, T-pieces and the like, do not affect the flow appreciably but strictures do.

<sup>23</sup> *Ann. Physik*, 12, 961 (1932); 14, 134 (1932).

<sup>24</sup> *Ibid.*, 41, 289 (1913); see also S. Weber, *Physica*, 6, 551 (1939).

<sup>25</sup> *Ann. Physik*, 29, 665 (1937).

<sup>26</sup> *Wien. Ber.*, 69, 713 (1874).

method of Fabry and Perot<sup>27</sup> for the determination of viscosity depends on the converse phenomenon, namely, the slow outflow of the gas from between two approaching plates. Two plates with known opposite electric charges are allowed to come together under their electrical attraction. The velocity of approach is measured optically by means of an interferometer and from this is calculated the velocity of efflux of the air. Precise measurements, as has already been noted, have been carried out at extremely low pressures by Gaede.<sup>28</sup>

Flow through porous media with wide pores has been treated as laminar viscous flow. It can be used to determine the total surface of the pores.<sup>29</sup>

(d) *Wide Tubes*: The Poiseuille formula holds only up to a certain velocity. This velocity is connected with the other conditions of the experiment by the "Reynolds number,"<sup>30</sup>

$$[R] = \frac{rW\rho}{\eta} \quad (27.23)$$

where  $r$  is the hydraulic radius of the tube, i.e.,  $r = \text{cross-section/periphery}$ . For circular tubes,  $r = D/4$ , where  $D$  is the tube diameter.<sup>31</sup> If  $[R] > 500$  to 3,000, the streamline flow described by the Poiseuille formula ceases and turbulent flow sets in.

In laminar (Poiseuille) flow the velocity is distributed parabolically over the cross-section of a circular tube, being zero at the wall and increasing proportionally to the square of the distance from the wall towards the axis.<sup>32</sup> In turbulent flow the average velocity is much more uniform over the cross-section, the drop to zero being restricted to a thin skin at the wall.

(28) **The Theory of the Molecular Pump. The Gaede Kinetic Heat Effect:** The fact that at very low pressures the flow through small openings is negligibly small has found an important technical application, aside from that in the investigations of molecular rays, in the Gaede<sup>1</sup> molecular pump which depends upon an application of the considerations of Section 24. Consider a horizontal channel of height small in comparison to the mean free path. The lower limiting surface is moved to the right in a horizontal direction with the velocity  $W_0$ . All the molecules colliding with the bottom plate acquire an excess horizontal component of velocity equal to  $W_0$ . If the channel is closed at each end, there is developed a pressure difference between the left and the right

<sup>27</sup> *Ann. Chim.*, **13**, 275 (1898).

<sup>28</sup> *Ann. Physik*, **41**, 337 (1915).

<sup>29</sup> M. Muskat, *The Flow of Homogeneous Fluids through Porous Media*, (New York: McGraw-Hill Book Co. Inc., 1937); J. L. Fowler and K. L. Hertel, *J. Appl. Phys.*, **11**, 496 (1940); R. R. Sullivan and K. L. Hertel, *ibid.*, p. 761.

<sup>30</sup> O. Reynolds, *Phil. Trans. Roy. Soc.*, **174**, 935 (1883).

<sup>31</sup> For circular tubes  $4[R]$  is frequently called the Reynolds number.

<sup>32</sup> Explicitly,  $W = 2\bar{W}\left(1 - \frac{4r^2}{d^2}\right)$ , where  $\bar{W}$  is the average flow speed and  $r$  the distance from the axis.

<sup>1</sup> W. Gaede, *Ann. Physik*, **41**, 337 (1913).

ends which, at the steady state, amounts to

$$\frac{B}{2} \frac{dp}{dx} \frac{1}{\sqrt{2\pi MRT}} = N_A c A \frac{W_0}{2} \quad (28.1)$$

The left hand side of this expression gives the amount of gas flowing down the pressure gradient to the left,  $B$  being the constant of Equation (27.8) which is dependent on the dimensions of the channel. The right hand side of the equation denotes the amount of gas piled up on the right through the cross-section of the channel  $A$ , as a result of the mean velocity  $\frac{1}{2}W_0$  received from the moving plate. If the channel is closed at each end, but the ends provided with wide inlet and outlet tubes, there will be a suction at the left and an expulsion of gas at the right provided that the pressure has first been reduced so far that the mean free path is large in comparison with the dimensions of the channel. In practice the space between two cylinders takes the place of the channel, the inner cylinder being rapidly rotated. A metal vane extends from the outer stationary cylinder nearly to the inner moving one. The gas between the cylinders is swept away from one side of the vane to the other side. Tubes are sealed to the outer cylinder on both sides of the vane, one serving as inlet and the other as outlet. As was observed at the beginning of this paragraph the space between the rotating cylinder and the vane need not be tightly packed if this space is small in comparison with the cross-section of the channel.<sup>2</sup>

While investigating his molecular pump, Gaede<sup>3</sup> was led to the discovery of a new effect. Since the action of the molecular pump increases the velocities of the molecules along one direction and decreases their velocities in the opposite direction, an object placed in the moving gas will experience a rise in temperature on the side toward which the molecules are hurled by the rotor and a corresponding decrease on the opposite side. Gaede placed two thin copper plates in the moving gas at right angles to the direction of motion and found, as he had predicted, that the forward plate was warmed and the other cooled. The observed temperature rise was of the expected order of magnitude. The theoretical treatment of the effect has been extended by Weber<sup>4</sup> who showed that the temperature change depends on the accommodation coefficient of the particular gas used. Rucker<sup>5</sup> has employed Weber's equations to calculate a number of accommodation coefficients from measurements of the Gaede effect.

(29) **The Motion of Foreign Particles under the Influence of a Constant Force:**<sup>1</sup> (a) *Small Particles:*<sup>2</sup> The motion of small foreign particles under a

<sup>2</sup> A pump utilizing the same principles as the foregoing, but embodying a number of mechanical improvements, has been designed by Holweck. Cf. L. Dunoyer, *Vacuum Practice*, p. 36.

<sup>3</sup> W. Gaede, *loc. cit.*, p. 369.

<sup>4</sup> *Z. Physik*, **24**, 267 (1924).

<sup>5</sup> *Ann. Physik*, **85**, 831 (1928).

<sup>1</sup> Throughout Section 29,  $w$  is used instead of  $|w|$ , for the magnitude of the velocity.

<sup>2</sup> See the comprehensive report of H. F. Mayer, *Jahrb. Radioakt. und Elektronik*, **18**, 201 (1921) for the views of Lenard. For others, see L. B. Loeb, *Fundamental Processes of Electrical Discharge in Gases* (New York: John Wiley and Sons, 1939), chapter I, part C.

constant force through a gas is of interest to many branches of physics. For example, in the conduction of electricity through gases the ions are impelled through the gas by the electric field. If these ions were in a vacuum and were acted upon by the constant force  $F$ , they would experience a constant acceleration  $a_x = F_x/m$  and their velocities would increase continually,

$$W_x = a_x t = \sqrt{2a_x x} \quad (29.1)$$

In a gas, however, they collide with the gas molecules, and it has already been proven that such collisions result in an equalization of the kinetic energy of the colliding bodies. On the average, therefore, upon colliding with the gas molecules the ions give up at least a part of the kinetic energy which they have obtained from the field of force and which is in excess of their normal thermal energy. The stationary state is reached when the mean energy loss of the ions per collision just equals the amount of energy they have gained since their last collision. The kinetic energy taken up by the gas molecules naturally increases their own kinetic energy and therefore the temperature of the gas. In this manner the frictional or resistance heat appears. This must be conducted away from the system if the process is to remain isothermal. In the following discussion the primed symbols will refer to the gas molecules and the unprimed to the foreign particles, in the present example, the ions.  $w_g$  will be used to indicate the mean thermal velocity ( $w_g = 2\sqrt{2kT/m\pi}$ ).

The formulae applicable to this case were first deduced by Riecke and later by Drude<sup>3</sup> with the aid of the assumption that each ion loses its excess kinetic energy completely at each collision (inelastic collisions). Then, according to Drude, the mean excess velocity in one direction which is added by the field of force is  $\frac{1}{2}a\bar{t}$  (zero at the beginning of the free path and  $a\bar{t}$  at the end). Here the thermal velocity which is also present plays no role since it is directed equally often to the right and to the left.  $\bar{t}$ , the mean time between successive collisions, is equal to the mean free path divided by the mean velocity, being approximately

$$\bar{t} = \frac{\Lambda}{\sqrt{\left(\xi + \frac{a\bar{t}}{2}\right)^2 + \eta^2 + \zeta^2}} \quad (29.2)$$

In the cases occurring in practice, the added velocity is small in comparison to the thermal velocity. Therefore

$$\bar{t} = \frac{\Lambda}{w_g} \quad (29.3)$$

and

$$W_x = \frac{1}{2m} \frac{F_x \Lambda}{w_g} = \frac{1}{2m} \frac{F_x \Lambda}{d^2 \pi N_A c 2\sqrt{2kT/m\pi}} F_x \quad (29.4)$$

<sup>3</sup> E. Riecke, *Wied. Ann.*, **66**, 376 (1898); P. Drude, *Ann. Physik*, **1**, 575 (1900). The application to ions in gases was made by L. Langevin, *Ann. chim. phys.*, **5**, 245 (1905).

The added velocity is seen to be proportional to  $F$ , the force. In this equation  $d$  signifies the sum of the radii of an ion and a gas molecule. Thus, the individually uniformly accelerated motions are reduced, as a result of the friction engendered by molecular collisions, to an average constant velocity proportional to  $F$ .

If, on the other hand, either the mean free path or the applied force is so large that the added velocity becomes large in comparison with the thermal velocity the motion between collisions can be considered as a motion with constant acceleration and negligible initial velocity. The result is

$$4 m' w_g' \sqrt{m} \quad (29.5)$$

According to Lenard, this expression should be multiplied by

$$(1 + 4m'/\pi m)(1 + 3m'/4m)^{-1} \quad (29.6)$$

It is seen that the resulting drift velocity  $W$  is proportional to the force  $F$ , as if the particle were moving in a viscous medium. Since  $\Lambda'$  is inversely proportional to the pressure, the resistance ( $F/\overline{W}$ ) is proportional to the pressure.

If the particle is large compared to the molecules, i.e.,  $r \gg r'$ , but still small compared to the mean free path, and has a mass large compared to that of the molecules, i.e.,  $m \gg m'$ , Equation (29.5) is reduced to

$$\overline{W}/F = (\frac{4}{3}\pi r^2)^{-1}(N_A c w_g')^{-1} \quad (29.7)$$

The resistance is therefore proportional to the cross-section of the particle and the pressure of the gas.

Throughout the foregoing discussion it has been assumed that the molecules are specularly reflected from the foreign body. This, of course, is only one of a number of possibilities. The other cases have been studied by Lenard and more thoroughly by Epstein.<sup>4</sup> Before proceeding to the other types of reactions between the particle and the gas molecules it is desirable to study in more detail the case of specular reflection. The resistance of the gas equals the momentum imparted to the sphere by the molecular impacts. This momentum can be divided into the part due to the impact of the molecule and that due to its rebound. It is then found that the latter part vanishes when summed over the sphere. This is so because of the spherical shape of the particle. Because of the higher relative velocity, more molecules hit the forward hemisphere of the particle than the reverse, and the relative momenta are larger. But the directions of the particles reflected from the forward hemisphere are distributed over the whole sphere; those molecules which hit the forward hemisphere a glancing blow near the equator impart a forward momentum to the sphere upon recoil. Similarly, those molecules hitting the backside of the particle near the equator provide a backward momentum upon reflection. Accordingly, the whole effect given by Equation (29.7) is due to momentum

<sup>4</sup> *Phys. Rev.*, 23, 710 (1924).

of impact. On the other hand the recoil momentum would not vanish in the case of a moving plane.

The next type of reaction between molecule and particle to be considered is as follows: The molecules adhere to the surface and do not "evaporate" until a short interval of time has elapsed. During this interval the particle has turned irregularly <sup>5</sup> (Brownian motion) so that, on the average, the molecules evaporate uniformly in all directions. The recoil momentum therefore cancels out and the result is the same as before.

With methods analogous to those used in Section 37 it can be shown that for a particle of arbitrary shape the factor  $\frac{4}{3}\pi r^2$  in (29.7) has to be replaced <sup>6</sup> by  $\frac{1}{4}\int (1 + \cos^2 \vartheta) dS$ , where  $dS$  is an element of the surface of the particle and  $\vartheta$  the angle its normal makes with the direction of motion.

The final case to be considered is that of diffuse reflection described by Lambert's cosine law (intensity  $\propto \cos \vartheta \sin \vartheta d\vartheta$ ). Two assumptions are still possible under this case. First, it might be assumed that the energy brought to any particular point on the sphere by impact must be removed by molecules hitting that point (thermally nonconducting sphere) or, secondly, that equalization of energy takes place throughout the sphere and all the molecules leave the sphere with the same average energy (perfect thermal conduction). In both cases there is a resultant recoil momentum, due to the fact that more molecules hit the forward side of the sphere than the reverse. The first assumption requires the insertion in Equation (29.7) of the factor  $\left(\frac{4}{3} + \frac{3\pi}{16}\right) / \frac{4}{3}$ , the second requires the factor  $\left(\frac{4}{3} + \frac{\pi}{6}\right) / \frac{4}{3}$ .

Miller and Landberg <sup>7</sup> have observed that the front of a small particle moving rapidly through a gas is at higher temperature than the other side, in analogy to the Gaede kinetic heat effect (Section 28).

(b) *Large Spheres. The Stokes-Cunningham Law:* For the case of the motion of large spheres (i.e., large in comparison with the mean free path), the velocity is obtained from Stokes's law, <sup>8</sup>

$$W = \frac{F}{6\pi r\eta} \quad (29.9)$$

which is derived from the hydrodynamic equations applicable to this case.

Here again the velocity is directly proportional to the force but it is no

<sup>5</sup> G. Breit, *Phys. Rev.*, **23**, 608 (1924).

<sup>6</sup> If the particle is considered as stationary and the gas as moving in the  $Z$ -direction with the speed  $W$ , the velocity distribution is given by (16.4), with  $W_x = W_y = 0$ . If this is developed into a power series in  $W$  and only the first two terms are retained, the result is

$$dN = N_0 \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{mw^2}{2kT}} \left(1 - \frac{m}{kT} \zeta W\right) d\xi d\eta d\zeta \quad (29.8)$$

The rest of the calculation is very similar to that given in the footnote of Section 37.

<sup>7</sup> P. H. Miller, Jr. and E. L. Landberg, *Amer. J. Phys.*, **10**, 20 (1942).

<sup>8</sup> G. Stokes, *Cambr. Phil. Soc. Trans.*, **9**, 5 (1856). Cf. also J. Weyssenhoff, *Ann. Physik*, **62**, 1 (1920).

longer inversely proportional to the cross-section or the density of the gas as was the case with small spheres. In the present case the velocity is inversely proportional to the first power of the radius of the particle. The physical difference between the two cases is as follows: In the first instance of the *small* particles (or ions), it was assumed that the motion of the particle had no effect on the motion of the molecules in front of it prior to the actual collision. The situation is analogous to the flow of molecules through an opening small in comparison to the mean free path where all the molecules go through the opening which would have collided with the same area of the wall had the opening not been present, since the presence of the opening in no way affects the motion of the molecules in front of the opening. Similarly, if the particle is small in comparison to the mean free path, it is hit by just as many molecules as would hit an imaginary surface of area  $\pi(r + r')^2$ , and in these collisions the molecules have the same velocity that they would have upon colliding with the imaginary surface. Therefore the amount of momentum given to the particle is proportional to  $\pi(r + r')^2$ . In Stokes's case, however, the motion of the gas molecules is changed throughout the entire surrounding region by the motion of the particle. That is to say, so many molecules are reflected from the particle that they might be said to prepare the molecules in front of them, due to their altered distribution of velocities. The entire body of gas in front of the particle has therefore a component of velocity parallel to the velocity of the particle. The extent of this region increases with the size of the sphere. It therefore follows that the momentum transferred to the particle is no longer proportional to its cross section, but increases only with the first power of  $r$ .

Naturally, there must be a transition between the two cases (proportional to  $1/r$  and  $1/r^2$ ) and Cunningham<sup>9</sup> tried to find it by taking into account the slip. He obtained the relation

$$W = \frac{F}{6\pi\eta r} \left( 1 + 1.63 \frac{\Lambda}{r} \right) \quad \text{or} \quad \left( 1 + \frac{1.63}{1 + f} \frac{\Lambda}{r} \right) \quad (29.10)$$

This would give a law of the desired form but the derivation is not rigorous, and other calculations give different results.<sup>10</sup>

With a finite coefficient of slip  $\eta/\eta_e$ , hydrodynamic analysis gives the equation<sup>11</sup>

$$W = \frac{F}{6\pi\eta r} \frac{1 + 3 \frac{\eta}{\eta_e r}}{1 + 2 \frac{\eta}{\eta_e r}} \quad (29.11)$$

<sup>9</sup> *Proc. Roy. Soc., A*, **83**, 357 (1910).

<sup>10</sup> L. W. McKeehan, *Physik. Z.*, **12**, 707 (1911).

<sup>11</sup> See, for example, W. Lamb, *Hydrodynamics* (4th ed.; London: Cambridge University Press, 1916), p. 593.



If the slip is small ( $\eta/\eta_e r < 1$ ), this approximates to

$$W = \frac{F}{6\pi\eta r} \left( 1 + \frac{\eta}{\eta_e r} \right) \quad (29.12)$$

where

$$\frac{\eta}{\eta_e} = 0.7004 \frac{2-f}{f} \Lambda \quad (29.13)$$

(The numerical coefficient 0.7004 appears because  $\eta$  is set equal to  $0.3502\rho w_s\Lambda$ ). This formula would seem to offer a transition to the value obtained from the gas theory for small spheres since for very small values of  $r$  the quotient  $(\eta/\eta_e r) \gg 1$  and therefore the resistance becomes, as it ought to be in this case, proportional to  $r^2$ . Actually, however, the series development is then not permissible and the exact formula (29.11) reduces for small values of  $r$  to  $W = F/4\pi\eta r$  which is in contradiction to the direct deduction of (a) and to experimental evidence. The reason<sup>12</sup> for this is due to the fact that in the hydrodynamical treatment the momentum is considered to be imparted to the particles only by the components of velocity parallel to the surface (friction). This reasoning demands that the transfer of impulse vanish at the forward and back poles of the sphere while in the kinetic treatment it is just these collisions with the poles which are most important. In the method of hydrodynamics this last effect disappears since the propagation of pressure throughout the whole fluid equalizes these differences which occur only on account of the discontinuous structure of the gas (finite free path). An interesting proof of (29.11) has been given by Epstein.<sup>13</sup> Using the general method of Section 16, he set the function  $P$  occurring in (16.9) constant. With the help of the relations (17.1), he found

$$f = f_0 \left\{ 1 - \frac{m}{kT} (u\xi + v\eta + w\zeta) + \frac{m^2}{2k^2T^2\rho^2} [(p_{xx} - p)\xi^2 + (p_{yy} - p)\eta^2 + (p_{zz} - p)\zeta^2 + 2p_{yz}\eta\zeta + 2p_{zx}\zeta\xi + 2p_{xy}\xi\eta] \right\} \quad (29.14)$$

with  $u, v, w$  as components of the bulk velocity of the gas. This leads to the hydrodynamical Equation (29.11).

Actually a measurement of the damping of vibrating spheres through a wide pressure range has led Knudsen and Weber to the equation<sup>14</sup>

$$W = \frac{F}{6\pi\eta r} \left( 1 + 0.68 \frac{\Lambda}{r} + 0.35 \frac{\Lambda}{r} e^{-1.85\frac{r}{\Lambda}} \right) \quad (29.15)$$

Shortly afterwards a similar result was obtained by Millikan<sup>15</sup> from an investigation of the motion of falling spheres. Further work gave him as the best

<sup>12</sup> Cf. R. A. Millikan, *Phys. Rev.*, **32**, 382 (1911); **21**, 217 (1923).

<sup>13</sup> *Loc. cit.*; see also R. A. Millikan, *Phys. Rev.*, **21**, 217 (1923).

<sup>14</sup> *Ann. Physik*, **36**, 981 (1911).

<sup>15</sup> *Brit. Ass. Rep.*, Dundee (1912), p. 410.

expression of his results<sup>16</sup> obtained from a study of the fall of oil drops in air, in which the ratio  $\Lambda/r$  was varied from 0.1 to 134, the relation

$$W = \frac{F}{6\pi\eta r} \left[ 1 + \frac{\Lambda}{r} (0.864 + 0.29e^{-1.52\frac{r}{\Lambda}}) \right] \quad (29.16)$$

For large spheres this becomes

$$W = \frac{F}{6\pi\eta r} \left( 1 + 0.864 \frac{\Lambda}{r} \right) \quad (29.17)$$

and for small spheres

$$W = \frac{F}{6\pi\eta r} 1.15 \frac{\Lambda}{r} \quad (29.18)$$

Millikan pointed out that if this is compared first with the exact formula (29.12) for large spheres and second with the formula obtained from the gas theory for small spheres, the first comparison shows that

$$0.864 = 0.7004 \frac{2-f}{f} \quad (29.19)$$

From this it is found that  $f$ , the fraction of the molecules which are "emitted," is 0.895, while about 10 per cent of the molecules are reflected. These figures are for oil drops in air. The coefficient for mercury droplets is 0.708 instead of 0.864 whence  $f = 1$ , for shellac, 1.078 ( $f = 0.79$ ). For oil drops in hydrogen there was found the value 0.815 ( $f = 0.925$ ), and in carbon dioxide, 0.82.

While the measurements with large spheres permitted the calculation of the accommodation coefficient,  $f$ , they gave no information as to whether the molecules are "reemitted," (i.e., leave the sphere only after a little time during which the sphere has rotated) or whether they are diffusely deflected (leave the surface of the sphere isotropically with a Maxwellian distribution of velocities) at the point at which they collided. The reason for this is that in the region  $r > \Lambda$  only tangential forces come into consideration and since in both of the above cases the departing molecules are distributed symmetrically about the normals to the surface, those tangential forces which are due to the departing molecules do not appear in either case. The entire force is due to the arriving molecules and those of the departing molecules which are elastically reflected. On the other hand, in the case of small particles (kinetic equation), it is the normal forces which are of significance. Millikan here compares his coefficient 1.154 with the magnitudes calculated by Lenard and Epstein for the same case. The latter are for the case of specular reflection and "re-emission," 1.575 and for diffuse reflection at the point of collision, 1.131. Since 10 per cent are reflected ( $1 - f = 0.1$ ) the remaining 90 per cent must obey the last named law which predicts the value 1.164 in comparison with the measured value 1.154.

<sup>16</sup> *Phys. Rev.*, 21, 217 (1923); 22, 1 (1923). Cf. also J. Mattauch, *Physik. Z.*, 25, 620 (1924); G. Mönch, *ibid.*, 34, 77 (1933).

Table VIII gives the values of the coefficients of external friction in c.g.s. units for a number of gases at 1 atm pressure and about room temperature. Maxwell's  $f$  is also listed.

TABLE VIII  
COEFFICIENTS OF EXTERNAL FRICTION

Gas	Surface	Coefficient of Ext. Friction	$f$
H <sub>2</sub> .....	Nickel <sup>1</sup>	110-140	—
Air.....	Nickel	80-100	—
CO <sub>2</sub> .....	Nickel	50-60	—
CO <sub>2</sub> .....	Old Shellac <sup>2</sup>	44	1
Air.....	Old Shellac	66	1
Air.....	New Shellac	97	0.79
Air.....	Polished Brass	75.4	—
Air.....	Mercury	66	1
Air.....	Oil	81.8	0.895
CO <sub>2</sub> .....	Oil	50	0.92
H <sub>2</sub> .....	Oil	—	0.925
He.....	Oil	—	0.875

<sup>1</sup> A. Timiriazeff, *Ann. Physik*, 40, 971 (1913).

<sup>2</sup> L. J. Stacey, *Phys. Rev.*, 21, 239 (1923); R. A. Millikan, *ibid.*, p. 217; K. S. van Dyke, *ibid.*, p. 250; Y. Isida, *ibid.*, p. 550.

(30) Other Measurements of the Accommodation Coefficient for Slip: A. van Itterbeek and his coworkers <sup>1</sup> have measured the slip in conjunction with viscosity measurements. A disk of quartz glass was oscillated in its own plane, with a stationary disk arranged at small distance from the oscillating disk, and parallel to it. The pressure of the surrounding gas was varied. In this way the following values were found.

VALUES OF THE COEFFICIENT OF  $\Lambda$  IN (24.4)

Gas	90°K	20°K	15°K
He.....	1.39	1.50	1.60
H <sub>2</sub> , D <sub>2</sub> .....	1.30	1.65	1.85

Keesom and Schweers <sup>2</sup> found slightly different values from thermomolecular pressure ratios in capillaries (Section 35), but confirmed the increase with falling temperature.

It must be stated that the calculation of  $f$  from the slip coefficient is not quite certain, because of the uncertainty of the numerical factor (unity or 0.7004, or 2/3) in front of  $(2 - f)/f \cdot \Lambda$ .

<sup>1</sup> A. van Itterbeek and O. van Paemel, *Physica*, 7, 273 (1940).

<sup>2</sup> *Ibid.*, 8, 676 (1941).

Direct experiments of Wood<sup>3</sup> and Knudsen<sup>4</sup> have shown that mercury atoms striking a glass surface are thrown back according to the cosine law. Baule<sup>5</sup> has attempted to give a quantitative theory for  $f$ ; however, his model does not correspond to our present knowledge of the forces between gas molecules and solids.

The theory is complicated by the fact that—contrary to the case of energy transfer—the details of the surface shape do influence the transfer of tangential momentum. To investigate the physics of the process, it would be necessary therefore to work with smooth surfaces of single crystals. Experiments by Ellett and Olson<sup>6</sup> have shown that cadmium and mercury atoms are reflected specularly from a clean rock salt surface but that sodium atoms are not reflected at all. Johnson<sup>7</sup> has found that hydrogen atoms are diffusely reflected from a number of crystal surfaces, provided that the temperature of the surface is high enough.

Estermann, Stern and Frisch<sup>8</sup> have investigated the diffraction of molecular beams of helium atoms by LiF surfaces and found both a specularly reflected beam (zero order spectrum) and higher orders, with apparently unexpected intensity distributions. Artmann<sup>9</sup> has explained the intensity distribution by treating the optical analogy, namely diffraction of light from a puckered surface, with a surface layer of different refractive index, the latter to represent the interaction energy between gas molecules and crystal surface. Inelastic reflections are also taken into account. These results have not yet been used to calculate the value of  $f$  for two parallel crystalline surfaces. For smooth microcrystalline surfaces, in which all microcrystals have the same crystallographic face in the surface, all the zero-order spectra would contribute to specular reflection ( $1 - f$ ), all higher-order spectra to diffuse reflection.

(31) **Heat Conduction at Moderate Pressures:** The calculations of thermal conductivity are, with one exception, entirely analogous to those of viscosity. In the previous case, the quantity transported, namely the momentum  $mW$  in the  $x$ -direction, had nothing to do with the velocity of transport  $w$  in the  $z$ -direction, and the effect of deviations from Maxwell's law noted in the preliminary remarks were slight. In the present case, however, the transported quantity is the kinetic energy  $\frac{1}{2}mw^2$ , and this is directly connected with the velocity of transport, which varies if the temperature gradient varies from point to point. The effect of this complication is to give one a quite incorrect equation in the course of the argument if, in the simplified procedure which will be used here, the modification of the distribution is not taken into

<sup>3</sup> *Phil. Mag.*, **30**, 300 (1915).

<sup>4</sup> *Ann. Physik*, **48**, 1113 (1915).

<sup>5</sup> *Ibid.*, **44**, 145 (1914).

<sup>6</sup> *Phys. Rev.*, **31**, 643 (1928).

<sup>7</sup> *J. Franklin Inst.*, **206**, 301 (1928).

<sup>8</sup> I. Estermann and O. Stern, *Z. Physik*, **61**, 95 (1930); R. Frisch and O. Stern, *ibid.*, **84**, 430 (1933); R. Frisch, *ibid.*, p. 433.

<sup>9</sup> *Ibid.*, **118**, 624, 659 (1941); **119**, 42, 137 (1942).

account.<sup>1</sup> The final result, however, is correct to the same degree, that is, to within a numerical factor, as in the case of viscosity. On the other hand, greater difficulties will present themselves in Section 40 in the discussion of radiator forces.

Consider two plane surfaces of infinite extent placed parallel to the  $xy$ -plane. Between them is situated a gas of such density that the mean free path is small in comparison to the distance between the surfaces,  $d$ . The upper surface is maintained at the temperature  $T_2$  and the lower at the temperature  $T_1$ . A linear temperature gradient will then be set up in the gas just as, when the surfaces were in motion, a linear velocity gradient was set up. In the layer of gas which is a distance  $z_0$  from the bottom plate the temperature is (approximately, see below)

$$T_0 = T_1 + \frac{\partial T}{\partial z} z_0 = T_1 + \frac{T_2 - T_1}{d} z_0 \quad (31.1)$$

The molecular density at the same layer is  $N_A c$  and the mean velocity of the molecules  $w_0$  is that determined by the temperature  $T_0$ . The number of molecules flowing downward through 1 cm<sup>2</sup> of this layer per second is, on the average,

$$N_A (c_+ w_+ / 6) \quad (31.2)$$

These molecules come from a layer higher by a distance equal to the mean free path,  $\Lambda$ .  $w_+$  and  $N_A c_+$  are respectively the mean velocity and density prevailing in the higher layer. Similarly, there move upward in the same time through unit area of the layer at  $E_0$

$$N_A (c_- w_- / 6) \quad (31.3)$$

molecules which come from a layer lower by one free path.

Since there is no mass motion of the gas at the steady state (convection currents due to gravity are eliminated by specifying that the colder plate is at the bottom) the number of molecules moving up must equal the number coming down in the same time, i.e.,

$$N_A (c_+ w_+ / 6) = N_A (c_- w_- / 6) \quad (31.4)$$

or the product  $cw$  must be constant throughout the gas. This is the false formula already referred to, since it would lead to the conclusion that  $cw^2$  is proportional to  $w$ , or that the pressure  $p (= \frac{1}{3} c M w^2$ ; p. 15) changes throughout the temperature gradient due to proportionality with  $w$  or  $\sqrt{T}$ . This result is erroneous. As a matter of fact the formula just deduced is applicable to the case of very low pressures where the collisions do not play a part in the process. At higher pressures there is no change in pressure along the temperature gradient (approximately, cf. Section 35). Hence the density is inversely proportional to the temperature ( $c \propto 1/T$ ).

As has already been noted, the fact neglected in the argument is that the

<sup>1</sup> This fallacy is pointed out with especial emphasis by M. von Smoluchowski, *Ann. Physik*, 35, 997 (1911).

velocities of the molecules are no longer equally distributed over all directions. On the contrary there is an excess component of velocity in the direction of the decreasing  $z$ . The equality of the number of molecules moving down to the number moving up is caused by the fact that although the density  $c_+$  of molecules coming from a higher layer is less, a larger proportion of these molecules moves downward. Accordingly  $c$  decreases with increasing  $z$  more rapidly than is to be expected from Equation (31.4) so that the pressure remains constant as set forth above.<sup>1a</sup>

In any case the energy transported by each molecule coming from above is

$$\frac{1}{N_A} E_+ = \frac{1}{N_A} \left( E_0 + \Lambda \frac{\partial E}{\partial z} \right) = \frac{1}{N_A} \left( E_0 + \Lambda C_v \frac{\partial T}{\partial z} \right) \quad (31.5)$$

where  $C_v$  is the molar heat capacity at constant volume. Similarly the energy transported by molecules coming upwards is

$$\frac{1}{N_A} E_- = \frac{1}{N_A} \left( E_0 - \Lambda \frac{\partial E}{\partial z} \right) = \frac{1}{N_A} \left( E_0 - \Lambda C_v \frac{\partial T}{\partial z} \right) \quad (31.6)$$

If  $\lambda$  equals the thermal conductivity, that is, the amount of heat flowing per second through unit area under a temperature gradient of  $1^\circ/\text{cm}$ , the total heat flow across unit area of the layer of gas under consideration is

$$\lambda \frac{\partial T}{\partial z} = \frac{cw}{6} 2\Lambda C_v \frac{\partial T}{\partial z} = \frac{1}{3} wc\Lambda C_v \frac{\partial T}{\partial z} \quad (31.7)$$

or

$$\lambda = \frac{1}{3} wc\Lambda C_v = \eta \frac{C_v}{M} \quad (\text{cf. Equation [21.5]}).^2 \quad (31.8)$$

This proportionality between thermal conductivity and coefficient of viscosity,

$$\lambda : \eta = C_v : M \quad (31.9)$$

is due to the fact that, in the first case, the flow of energy  $C_v T$  is measured by  $\lambda(\partial T/\partial z)$  and in the second case, the flow of the momentum  $MW$ , is measured by  $\eta(\partial W/\partial z)$ , and that the mechanism of transport in the two cases is the same. An exact calculation by Chapman (Section 17) gives for monatomic, spherical molecules exerting an arbitrary central force the value

$$\lambda = 2.5 \frac{C_v}{M} \eta \quad (31.10)$$

<sup>1a</sup> E.g., a factor

$$1 + \frac{1}{2} \frac{\Lambda}{T} \cos \vartheta \frac{\partial T}{\partial z}$$

multiplied into a spherically symmetric distribution, would give the desired result, where  $\vartheta$  is the angle between the direction of the temperature gradient and the velocity of the molecule. For a more refined correction see (37.2).

<sup>2</sup> It follows from Equation (31.8) that the thermal conductivity of a gas is independent of the pressure, subject to the same limitations as the analogous statement for the viscosity. Measurements by H. Gregory and C. T. Archer (*Phil. Mag.*, **1**, 593 [1936]) have confirmed this prediction of the theory; see also Section 33.

According to Enskog (*loc. cit.*) for rigid spheres

$$\lambda = 2.522 \frac{C_v}{M} \eta \quad (31.11)$$

where  $\eta$  is given by (21.6). For rigid spheres with attractive forces the Sutherland correction (cf. [13.10] and [21.11]) is somewhat greater for  $\lambda$  than for  $\eta$ , so that the term  $1 + 0.036 C/T$  appears in the denominator of (31.11).<sup>3</sup> For a monatomic gas, Equation (31.11) holds down to the lowest temperatures as long as the gas can be treated as ideal.<sup>4</sup> Ubbink and de Haas<sup>5</sup> have measured the heat conductivity of helium down to 1.62°K and find that the temperature dependence agrees with de Boer's theory. (See also Section 22). The experimental values of the numerical factor lie, for the rare gases at room temperature, between 2.42 and 2.59.

Hirschfelder and his coworkers<sup>5a</sup> have calculated the temperature dependence of heat conductivity according to the Chapman-Enskog theory, using the form of the interaction energy as in the case of viscosity, (Section 21), and have compared their results with the precision measurements of Johnston and his coworkers.<sup>5b</sup> The agreement for polyatomic molecules is not very good, which they ascribe to the failure of Equation (31.11) because of slow energy exchange (Section 20).

The increase by the factor 2.5 is caused, according to Eucken,<sup>6</sup> by the fact that those molecules which have an exceptionally high energy content transport this energy exceptionally quickly. In the analogous case of the transport of momentum this is not the case for the reasons just discussed. In the approximate deduction using the average speed  $w$  this fact also does not enter into the expression. The exact result, however, is that the mean velocity of the transport of energy is increased over that of momentum. The plausible assumption may now be made that the rotational energy possessed by any one molecule at a given instant is independent of the simultaneous value of the translational energy, so that a molecule may have a large rotational energy without possessing at the same time a particularly large velocity of translation. It is evident that a molecule in such a state would not have an increased speed of transport of energy and the reason for the factor 2.5 is therefore removed so that for diatomic molecules for which  $C_{vt} = \frac{3}{2}R$  is the translational heat capacity, and  $C_{vr} = R$  that of rotation,

$$\lambda = \left( 2.5 \times \frac{3}{2} + 1 \times 1 \right) \frac{R}{M} \eta = \frac{19R}{4M} \eta = 1.9 \frac{C_v}{M} \eta \quad (31.12)$$

<sup>3</sup> See, on the other hand, S. W. Milverton, *Phil. Mag.*, 17, 397 (1934).

<sup>4</sup> J. de Boer, *Physica*, 10, 348 (1943).

<sup>5</sup> *Ibid.*, p. 464.

<sup>5a</sup> J. O. Hirschfelder, R. B. Bird and E. L. Spotz, *Trans. Am. Soc. Mech. Eng.*, 71, 921 (1949).

<sup>5b</sup> W. J. Taylor and H. L. Johnston, *J. Chem. Phys.*, 14, 219 (1946); H. L. Johnston and E. R. Grilly, *ibid.*, 14, 233 (1946).

<sup>6</sup> *Physik. Z.*, 14, 324 (1913).

A compilation of the experimental data for the diatomic gases  $H_2$ ,  $N_2$ ,  $O_2$ , and  $NO$  gives values between 1.97 and 1.87. In this deduction it is assumed that the rotational energy of a molecule comes to equilibrium with the colder layer to which it has penetrated just as quickly as does the translational energy (see however, Section 20).

Pidduck<sup>7</sup> has attempted to calculate the heat exchange of a rotating molecule using the rigorous method of Chapman (p. 63). In order to retain the simplifications of a spherical molecule and at the same time to have the possibility of the exchange of energy of rotation, he assumes the molecules to be perfectly rough hard spheres. The effect of their being rough is to reverse the relative velocities of their points of contact upon collision. The radius of gyration of the molecule, or the ratio of this quantity to the molecular diameter then enters the formula aside from the molecular diameter and mass which regulate the number of collisions. If the entire mass of the molecule were concentrated at its center, this ratio would equal zero. For a homogeneous solid sphere it is  $2/5$ , and for a sphere whose mass is concentrated in the outermost shell  $2/3$ . The corresponding number with which the factor 2.5 of Equation (31.12) is to be replaced is, for the three cases, 1.85,  $\sim 1.85$  and 1.71, which are in close agreement with Eucken's results.

Chapman<sup>8</sup> has generalized the model still further by considering a non-spherical shape of the diatomic molecule. To do this he assumes that the radius upon collision depends upon the velocities and orientations of the colliding molecules, the radius of gyration, however, is maintained constant.

With the purpose of including the effect of vibrational energy on heat conduction, Eucken next assumed that that part of the heat capacity due to vibrational energy  $C_v$  is to be taken into account by assuming that upon collision those components which are in the direction of motion are, in a certain sense, coupled with the velocity of the molecule so that the factor 2.5 holds also for this case but not for the other directions. As an example the equation for  $Cl_2$  is found to be

$$\frac{\lambda M}{\eta C_v} = \frac{\left(2.5 \times \frac{3}{2} + 1 \times 1\right) R + \left(\frac{2.5}{3} + \frac{2}{3}\right) C_v}{\left(\frac{3}{2} + 1\right) R + C_v} = 1.8 \quad (31.13)$$

in comparison with the experimental value of 1.803.

Some gases, however ( $CO$ ,  $CO_2$ ,  $SO_2$ ,  $H_2S$ ,  $H_2$ ), behave as if the exchange of the energies of rotation and vibration were not rapid enough to take part in the conduction of heat (see Section 20).

Ubbelohde<sup>9</sup> has treated the influence of slow energy exchange between

<sup>7</sup> *Proc. Roy. Soc., A*, **101**, 101 (1922), following a proposal of G. H. Bryan, *Brit. Assoc. Rep.*, **83** (1894).

<sup>8</sup> S. Chapman and W. Hainsworth, *Phil. Mag.*, **48**, 593 (1924).

<sup>9</sup> *J. Chem. Phys.*, **3**, 219, 362 (1935); K. Schäfer, W. Rating and A. Eucken, *Ann. physik*, **42**, 176 (1942) for the cylindrical case.



translation and rotation on the one hand, and vibration on the other. Molecules in different quantum states of internal vibrations can be treated formally as different kinds of molecules. If a molecule at a given place happens to undergo a collision which is effective in affecting its internal energy and adjusts it to the value appropriate to the particular place, the future motion of this molecule can then be considered as a diffusion until some other effective collision takes place elsewhere. The result for the heat flow between two plates at distance  $l$  per square centimeter is given by

$$A \frac{T_2 - T_1}{l} \cdot \frac{\eta}{M} (2.5 \times \frac{3}{2}R + C_{vr} + C_s) \times \left( 1 + \frac{2C_s}{2.5 \times \frac{3}{2}R + C_{vr}} \frac{1}{B} \frac{e^B - 1}{e^B + 1} \right)^{-1} \quad (31.14)$$

the expression in the second set of parentheses being the correction factor;  $B$  is defined by

$$B^2 = \left( \frac{C_s}{2.5 \times \frac{3}{2}R + C_{vr}} + 1 \right) \frac{l^2}{D\tau'} \quad (31.15)$$

where  $D$  is the coefficient of self diffusion (Section 42), and  $\tau'$  is the "relaxation time" for the exchange of energy between internal and external degrees of freedom (see Section 20). It has been assumed that no internal energy is exchanged at the plates.  $B$  is proportional to  $l/\Lambda$ , and hence the correction is not independent of the density. If, for  $\text{CO}_2$  at  $0^\circ\text{C}$  and 1 atm,  $D = 0.1/\text{cm}^2 \text{ sec}$ ,  $C_{vr} = R$ ,  $C_s = 1.7$ ,  $\tau' = 0.37 \times 10^{-5} \text{ sec}$ , the correction factor is  $1.152^{-1}$ ,  $1.148^{-1}$ ,  $1.05^{-1}$  and  $1.005^{-1}$  for a distance  $l = 3 \text{ mm}$  and pressures of 0.1, 1, 10 and 100 mm of mercury respectively.

Heat conductivity at pressures up to 90 atm has been measured by Sellschop.<sup>10</sup> Theoretical expressions are given by Enskog<sup>11</sup> and by Rocard.<sup>12</sup>

Important uses of heat conductivity measurements as a laboratory tool, based on (31.13), have been developed for the analysis of certain special gas mixtures, namely those in which the components have the same molecular size and molecular forces, in short, the same free path and the same mass. Hydrogen is made of two kinds of molecules called para-hydrogen and ortho-hydrogen, which are distinguished by nuclear spin and rotational states and which do not easily go over into each other. Because of their difference in rotational states, they have different rotational heat capacities  $C_r^{(1)}$  and  $C_r^{(2)}$  at intermediate temperatures. In a mixture containing the mole fraction  $x$  of (1) the conductivity is proportional to

$$(2.5 \times \frac{3}{2}R + C_r^{(1)})x + (2.5 \times \frac{3}{2}R + C_r^{(2)})(1 - x) \quad (31.16)$$

The apparatus is standardized with a mixture of known composition.<sup>13</sup>

<sup>10</sup> *Forsch. Geb. Ing. Wiss.*, 5, 162 (1934); see also, Wargrafitk, *Tech. Phys.* USSR, 4, 341 (1937).

<sup>11</sup> *Sven. Vetenskap. Handl.*, 63, No. 4 (1922).

<sup>12</sup> *Ann. physique*, 8, 5 (1927); 10, 345 (1928).

<sup>13</sup> K. F. Bonhoeffer and P. Hartek, *Z. physik. Chem.*, B, 4, 113 (1929); A. Farkas, *Ortho-*

For a mixture of isotopes (same  $C_v$  and  $\Lambda$ , but different masses) the formula is more complicated at low temperatures, but use of conductivity methods in a calibrated apparatus is very convenient.<sup>14</sup>

The thermal conductivity of mixtures is no more to be calculated additively from the corresponding values for the pure components than is the viscosity, since both depend upon the mean free path and this magnitude for one species of molecules is influenced by the presence of another species (Equation [11.15]). In analogy to (23.7) the exact calculation of Enskog gives, for elastic spheres, if there are no diffusion processes,

$$\lambda = \frac{\lambda' \left(1 + \beta_I' \frac{c}{c'}\right) + \lambda'' \left(1 + \beta_I \frac{c'}{c}\right) + A_I}{\left(1 + \beta_I \frac{c'}{c}\right) \left(1 + \beta_I' \frac{c}{c'}\right) - \frac{A_I^2}{4\lambda\lambda'}} \quad (31.17)$$

$$\text{where} \quad \beta_I = \left(\frac{d + d'}{2d}\right)^2 \sqrt{\frac{2m'}{m + m'} \frac{30m^2 + 16mm' + 13m'^2}{8(m + m')^2}} \quad (31.18)$$

$$= \left(\frac{d + d'}{2d'}\right)^2 \sqrt{\frac{2m}{m + m'} \frac{13m^2 + 16mm' + 30m'^2}{2(m + m')^2}} \quad (31.19)$$

$$A_I = 27\sqrt{2\lambda\lambda'} \frac{(d + d')^2}{16dd'} \frac{(mm')^{5/4}}{(m + m')^{5/2}} \quad (31.20)$$

Senftleben<sup>15</sup> has found that the thermal conductivity of a mixture of hydrogen and mercury vapor is changed if the mixture is radiated by light of wavelength 2537 Å. Cario and Franck<sup>16</sup> have shown that under such circumstances the hydrogen is partially dissociated by collisions of the second kind with mercury atoms excited by the ultraviolet light. The change in the thermal conductivity of the mixture therefore is due to a change in the composition of the mixture, part of the molecular hydrogen being converted into atomic hydrogen.

Long before this, Langmuir<sup>17</sup> used the increased conductivity of heat from a tungsten filament heated in hydrogen as a measure of dissociation of the hydrogen molecules into atoms.

(32) **Heat Conduction at Low Pressures:** Warburg<sup>1</sup> concluded that, at low pressures, there must take place a temperature discontinuity at the walls, in analogy to the slip. Smoluchowski<sup>2</sup> has studied the phenomenon experimentally. *hydrogen, Parahydrogen and Heavy Hydrogen* (London: Cambridge University Press, 1935), Part I, chap. 3.

<sup>14</sup> A. Farkas and L. Farkas, *Proc. Roy. Soc., A*, **144**, 467 (1934); A. Farkas, *op. cit.*, Part II, chap. 2.

<sup>15</sup> *Z. Physik*, **32**, 922 (1925).

<sup>16</sup> *Ibid.*, **11**, 161 (1922); **12**, 162 (1922).

<sup>17</sup> *J. Am. Chem. Soc.*, **34**, 860 (1912).

<sup>1</sup> A. Kundt and E. Warburg, *Pogg. Ann.*, **156**, 177 (1875).

<sup>2</sup> *Wied. Ann.*, **64**, 101 (1898); *Wien. Ber.*, **107**, 304 (1898); **108**, 5 (1899); cf. also *Ann. Physik*, **35**, 983 (1911).

mentally and has given it a theoretical explanation. Knudsen<sup>3</sup> has worked extensively with it; the work of others will be cited later. The treatment is formally identical with that of viscosity. Monatomic gases will first be discussed.

At low pressures, at which there are no collisions between molecules in the regions between the plates, formula (31.4) for the number of molecules moving upwards on the one hand and downwards on the other, which was found incorrect for dense gases, is valid, since diffuse collisions with the plate enforce a Maxwellian distribution of velocities. That is,

$$N_A(c_+ w_+/6) = N_A(c_- w_-/6) \quad (32.1)$$

where  $N_A c$  is the number of molecules per cc. Assuming complete heat exchange between molecule and plate, the amount of energy brought to the lower plate by a molecule coming from above is

$$\frac{1}{N_A} C_v T_2 \quad \text{or} \quad \frac{1}{N_A} \int_0^{T_2} C_v dT \quad (32.2)$$

if  $C_v$  varies with  $T$ . A corresponding equation holds for the molecules moving upwards. The flow of heat per sq cm is then given by

$$\frac{cw}{6} C_v (T_2 - T_1) \quad (32.3)$$

The more exact calculation gives, upon substituting for  $w$ ,

$$\frac{1}{T_1 + T_2} (T_2 - T_1) \quad (32.4)$$

This formula has been applied to the measurement of low pressures by means of the hot wire manometer (Pirani gauge) in which the heat conducted away from a hot wire is measured by noting the input of electrical energy.

In the case just discussed, there does not exist a temperature gradient, but the gas between the plates is at the uniform (average) temperature  $\sqrt{T_1 T_2}$ . If there exists an accommodation coefficient  $f'$  (e.g., if the fraction  $f'$  of the molecules colliding with a plate take on the temperature of the plate, while the fraction  $1 - f'$  does not undergo an energy change), Equation (32.4) has to be multiplied by  $f'/(2 - f')$  if both plates have the same accommodation coefficient, and by  $f'$ , if the accommodation coefficient of one is  $f'$ , and that of the other is unity.

In the case of intermediate pressures, the energy transferred to unit area of the plate by the fraction  $f'$  of the molecules is

$$f' \frac{cw}{6} \Delta E' \quad (32.5)$$

<sup>3</sup> *Ibid.*, 34, 593 (1911).

where  $\Delta E' = C_v \Delta T'$  and is the difference between the energy prevailing at a layer a distance  $\Lambda$  away from the plate and the energy corresponding to the temperature of the plate itself.

The energy transfer must equal the flow of heat through the interior of the gas. Therefore, according to (31.8),

$$f' \frac{cw}{6} C_v \Delta T' = \frac{cw}{3} \Lambda C_v \frac{\partial T}{\partial z} \quad \cdot \frac{\partial T}{\partial z} \quad (32.6)$$

$\partial T / \partial z$  may be evaluated from the fact that the temperature difference

$$(T_2 - \Delta T') - (T_1 + \Delta T') = T_2 - T_1 - 2\Delta T' \quad (32.7)$$

is distributed over the distance  $d - 2\Lambda$ , whence

$$\frac{\partial T}{\partial z} = \frac{T_2 - T_1}{d + 2 \frac{f'}{f'}} \quad (32.8)$$

and the conduction of heat <sup>4</sup> is given by

$$\lambda \frac{\partial T}{\partial z} = \lambda \frac{T_2 - T_1}{d + 2 \frac{2 - f'}{f'} \Lambda} \quad (32.9)$$

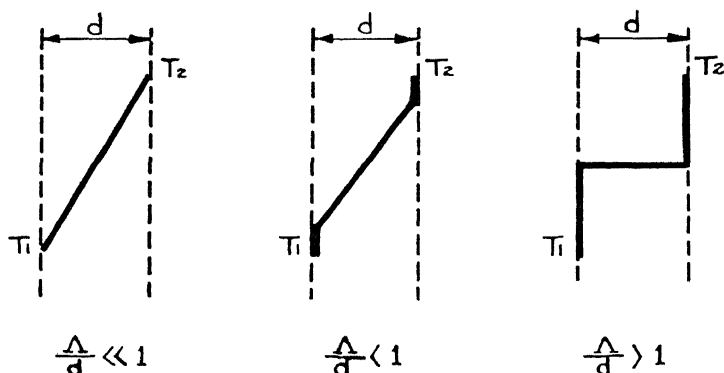


FIG. 25. Temperature Distribution Between Plates at Different Pressures.

The temperature discontinuity at the bottom plate is therefore

$$\Delta T'' = \frac{1}{2} [\Delta T' + (1 - f') \Delta T' + f' \cdot 0] = \frac{2 - f'}{5} \Delta T' \quad \frac{2 - f'}{f'} \Lambda \frac{\partial T'}{\partial z} \quad (32.10)$$

<sup>4</sup> The decrease in flow of heat caused by the temperature discontinuity at the walls is the cause of the good insulating properties of porous substances. This is of great technical importance in lagging and packing between walls. The effect is large since the air spaces are so subdivided that  $d$  is not large in comparison with  $\Lambda$ . M. von Smoluchowski, *Bull. Ac. Krak.*, 129 (1910).

The factor by which  $\partial T/\partial z$  must be multiplied to obtain  $\Delta T''$  is known as the coefficient of temperature discontinuity (Temperatursprung-koeffizient). It is here shown to be  $[(2 - f')/f']\Lambda$  and the more exact calculation confirms this value. For the case of two plane surfaces, Maxwell's assumption (p. 93) is equivalent to the postulate that all the molecules colliding with the surface rebound at the mean temperature  $T$ , where

$$T - T_1 = (1 - f')(T_0 - T_1) \quad (32.11)$$

and  $T_0$  is their temperature just before collision with the surface. On the other hand Smoluchowski<sup>5</sup> has shown that there is a difference in the case of the flow of heat between two concentric cylinders. The experiments seem to contradict the assumption that all the reflected molecules have the same temperature.

### (33) Measurement of Heat Conduction and Accommodation Coefficients:

There are essentially three methods of measuring heat conduction in gases. The first determines the time rate of cooling of a hot system immersed in a gas. This is the oldest method (Newton) but it has been taken up again recently.<sup>1</sup> In the second method<sup>2</sup> the gas is contained between large horizontal plates, heat is supplied continuously and the measurements are made when a stationary state is reached. This procedure has the advantage of few corrections, but needs a complicated apparatus. By using parallel plates, with the upper plate at the higher temperature, convection currents are avoided.

The third method, due to Schleiermacher<sup>3</sup> and significantly improved by Eucken, is the most popular. The apparatus consists of a cylindrical tube (glass or, better, metal), kept at constant temperature and filled with the gas to be investigated. A wire, to be heated electrically, runs along the axis of the tube. The resistance of the wire and the current are measured exactly. The amount of Joule heat developed in the wire and which is conducted away by the gas is then known. The temperature of the wire is determined from its resistance, that of the outer tube being fixed. The known heat developed per second and conducted away by the gas is given by a geometrical factor<sup>4</sup> multiplied by the temperature difference between wire and tube and the heat conductivity of the gas, which can therefore be found. Corrections must be

<sup>5</sup> *Ann. Physik*, **35**, 983 (1911). In this article as in Knudsen's, there will be found a discussion of heat flow in vessels of different shapes. Smoluchowski has shown that  $\Lambda$  in (32.9) and (32.10) should be multiplied by  $15/4\pi$ . See also E. Fredlund, *Ann. Physik*, **28**, 319 (1937).

<sup>1</sup> M. Curie and A. Lepape, *J. Phys. Radium*, **2**, 392 (1931).

<sup>2</sup> E. O. Hercus and T. H. Laby, *Proc. Roy. Soc., A*, **45**, 190 (1918); E. O. Hercus and D. M. Sutherland, *ibid.*, **A**, **145**, 599 (1934).

<sup>3</sup> *Wied. Ann.*, **34**, 623 (1888); **36**, 346 (1889); A. Eucken, *Ann. Physik*, **34**, 190 (1911); *Physik. Z.*, **12**, 1102 (1911); S. Weber, *Ann. Physik*, **82**, 479 (1927).

<sup>4</sup> Consider a cylindrical ring of height  $l$  cm, radius  $R$  and thickness  $dR$ . If the temperature at the outer surface is  $T$ , at the inner  $T + dT$ , the radial heat flow outward is per second

$$q = -2\pi Rl\lambda \frac{dT}{dR} \quad (33.1)$$

$2\pi Rl$  being the area of the inner mantle. But in the stationary state the same amount of

made for heat losses through the ends and from radiation. The first can be determined (or even compensated) with a similar tube of different length <sup>5</sup> (Eucken), and the latter is calculated or found by experiments in vacuo. A disturbing factor is the appearance of convection currents, which are absent at low pressures but become more important at normal pressures. According to Eucken, they can be avoided by making the tube sufficiently narrow (viscosity then prevents convection).

To determine  $f'$ , the following methods are available:

(a) <sup>6</sup> The heat transfer at different pressures from 1 atm down is governed by (32.8); as  $\Lambda$  is proportional to  $1/P$ , it can be calculated from experimental data by (21.7); thus,

$$\eta = \frac{5}{16} \left( \frac{2MRT}{\pi} \right)^{\frac{1}{2}} C\Lambda = \frac{5}{16} \left( \frac{2M}{\pi RT} \right)^{\frac{1}{2}} p\Lambda \quad (33.4)$$

so that the heat transported through a unit area is

$$q = \lambda \frac{T_2 - T_1}{d} \left[ 1 + 2 \frac{f'}{f} \frac{16}{5} \left( \frac{RT}{2M} \right)^{\frac{1}{2}} \frac{\eta}{d} \frac{1}{p} \right]^{-1} \quad (33.5)$$

If  $(T_2 - T_1)/qd$  is then plotted against  $1/p$ , a straight line is obtained, which gives  $1/\lambda$  for the intercept with the ordinate (i.e., for  $1/p = \infty$ ), while the slope gives the factor of  $1/p$ . For the usual cylindrical arrangement  $1/d$  must be replaced by a different geometrical factor. For the central thin wire only the accommodation at the wire matters, as in case (b) below.

To eliminate the influence of the accommodation coefficient Kannuluik and Martin <sup>7</sup> use a thick central rod. Ubbink and de Haas <sup>8</sup> have made this method applicable to very low temperature.

(b) It is possible to work at pressures so low that all the dimensions of the apparatus are small compared to the mean free path.<sup>9</sup> Then the heat transfer (32.4) is to be multiplied by  $f'/(2 - f')$  if both plates have the same accommodation coefficient, and by  $f'$  if one is rough and one only does not give complete exchange (as mentioned earlier).

heat  $q$ , must flow through every concentric cylindrical surface. Therefore,

$$\frac{q}{2\pi\lambda l} \frac{dR}{R} = -dT \quad (33.2)$$

and

$$\frac{q}{2\pi\lambda l} \ln \frac{R_e}{R_i} = T_i - T_e \quad (33.3)$$

where  $R_e$  is the inner radius of the tube,  $R_i$  the radius of the wire, and  $T_e$  and  $T_i$  are the corresponding temperatures.

<sup>5</sup> G. C. Sherratt and E. Griffiths, *Phil. Mag.*, 27, 69 (1939), use auxiliary heaters.

<sup>6</sup> M. von Smoluchowski, *Wied. Ann.*, 64, 101 (1898); F. Soddy and A. T. Berry, *Proc. Roy. Soc., A*, 83, 254 (1910); 84, 576 (1911); C. T. Archer, *Phil. Mag.*, 19, 901 (1935).

<sup>7</sup> *Proc. Roy. Soc., A*, 144, 496 (1934).

<sup>8</sup> *Physica*, 10, 451 (1943).

<sup>9</sup> M. Knudsen, *Ann. Physik*, 34, 591 (1934).

For a thin wire in a wider tube, it is very improbable that a molecule leaving the wire and striking the wall of the tube will be thrown back to the wire; instead it will strike another place on the wall of the tube and so be thrown back and forth a number of times before it returns to the wire. Therefore, if  $f'$  is not exceptionally small at the wall, only the accommodation at the wire matters and the heat transported is

$$2\pi r l \times C \left( \frac{RT}{2M\pi} \right)^{\frac{1}{2}} (C_v + \frac{1}{2}R)(T_2 - T_1)f' \quad (33.6)$$

The term  $C_v + \frac{1}{2}R$  appears because the average kinetic energy in a beam is  $2R = \frac{3}{2}R + \frac{1}{2}R$  (see Equation [35.17]). Thomas and Olmer have worked out the corrections for this case.<sup>10</sup>

Equation (33.6) has been used to measure the heat capacities of gases,<sup>11</sup> assuming a value of  $f'$ . It is best to make relative measurements only; then

$$\frac{q}{T_2 - T_1} \bigg/ \frac{q'}{T_2' - T_1'} = \left( \frac{T}{M} \right)^{\frac{1}{2}} (C_v + \frac{1}{2}R) \bigg/ \left( \frac{T'}{M'} \right)^{\frac{1}{2}} (C_v' + \frac{1}{2}R) \quad (33.7)$$

Eucken<sup>12</sup> has developed a method which permits  $C_v$  and  $f'$  to be measured simultaneously. The thin wire is replaced by a platinum ribbon, a few millimeters wide. The gas pressure is several thousandths of a millimeter of mercury, so that  $\Lambda$  is about 1 cm. In front of and parallel to the ribbon, 1 mm distant, is a wire of about  $\frac{1}{16}$  mm in diameter which is bombarded on one side by molecules coming from the ribbon, on the other side by those coming from the wall. The wire is so thin that it does not cast an appreciable "shadow" on the ribbon. From the heat received by the wire it is possible to calculate the average energy of the molecules just coming from the ribbon.

Another method<sup>13</sup> uses such pressures that the mean free path is short compared with the diameter of the tube, but long compared with that of the (extremely thin) wire. The argument is then very similar to the one used for flow through orifices small compared with  $\Lambda$  (p. 95). The molecules hitting the wire have had their last collision at a distance of about  $\Lambda$ , but the molecules making up the gas at a distance  $\Lambda$  from the wire come only to a very small fraction ( $2r/2\pi\Lambda$ ) from the wire, the rest coming from the interior of the gas. Therefore, the properties of the gas in this region are practically uninfluenced by the presence of the hot wire. Arguing step by step, the temperature drop is found to be limited practically to the distance  $\Lambda$  from the wire and that the rest of the gas is at the temperature of the tube-wall. Therefore, the formula

<sup>10</sup> L. B. Thomas and F. Olmer, *J. Am. Chem. Soc.*, **64**, 2190 (1942); **65**, 1036 (1943).

<sup>11</sup> A. Eucken and A. Bertram, *Z. physik. Chem.*, **B**, **31**, 361 (1936); W. Hunsmann, *ibid.*, **39**, 23 (1938); G. B. Kistiakowsky and F. Nazmi, *J. Chem. Phys.*, **6**, 18 (1938).

<sup>12</sup> A. Eucken and H. Krome, *Z. physik. Chem.*, **B**, **45**, 175 (1940); A. Eucken and B. Sarstedt, *ibid.*, **B**, **50**, 143 (1941). For a method of discovering the formation of double molecules, see: K. Schäfer and O. R. Foz Gazulla, *ibid.*, **B**, **52**, 299 (1942); O. R. Foz Gazulla and S. Senent Pérez, *ibid.*, **193**, 162 (1944).

<sup>13</sup> M. Knudsen, *loc. cit.*





cient. Figure 26, which is reproduced from a paper by Thomas and Olmer,<sup>2</sup> shows the majority of the available measurements of accommodation coefficients as functions of the temperature of the "hot" wire, the outer temperature being 30°C. The most important quantity for the classification of the results is the duration of the contact between gas molecule and wall. Langmuir<sup>3</sup> had assumed that any gas molecule reaching a solid surface is condensed and re-evaporates later, with an average energy corresponding to the temperature of the surface. However, it now seems certain that, depending on conditions, the time of contact may vary from  $10^{-13}$  sec ("collision") up to a rather long time. The time diminishes markedly with increasing temperature, so that a molecule which is adsorbed at a certain surface at low temperature and later re-evaporates, may at higher temperature rebound from the same surface within a few times  $10^{-13}$  sec.<sup>4</sup>

Next, a distinction must be made between the accommodation for translational (and probably rotational) energy on the one hand, and internal (or probably only vibrational) energy on the other hand. The accommodation for translational energy can best be studied in monoatomic gases, which possess no other energy. If the atom remains on the surface for a time appreciably longer (say ten times) than the collision time, i.e., it is actually adsorbed, it will re-evaporate with an energy corresponding to the surface temperature, i.e.,  $f' = 1$ . Mercury on platinum, for example, shows this effect at lower temperatures (Fig. 26, curve marked 2). Keesom and Schmidt<sup>5</sup> found  $f' = 1$  for  $H_2$  and Ne between 12°K and 20°K where adsorption should be strong.

For gases which are not appreciably adsorbed, it follows from elementary mechanics (classical and quantum) that a light particle hitting a heavy one will transfer only a small part of its energy.<sup>6</sup> The best exchange should be

<sup>2</sup> *J. Am. Chem. Soc.*, 65, 1036 (1943).

<sup>3</sup> *Ibid.*, 39, 1848 (1917).

<sup>4</sup> J. K. Roberts, *Some Problems on Adsorption* (London: Cambridge University Press, 1939); A. R. Miller, *The Adsorption of Gases on Solids* (Cambridge University Press, 1949).

<sup>5</sup> *Physica*, 3, 590, 1085 (1936); 4, 828 (1937).

<sup>6</sup> Consider a sphere of mass  $M$  at rest hit head on by another sphere of mass  $m$  and velocity  $w_0$ . Head on collision is of course, most favorable to energy transfer. We have, first, the principle of conservation of motion of the common center of gravity of the two spheres. Calling the velocities after collision  $W$  and  $w_1$ , we get

$$M \cdot 0 + mw_0 = MW + mw_1 \quad (34.1)$$

The conservation of energy gives

$$\frac{1}{2}M0^2 + \frac{1}{2}mw_0^2 = \frac{1}{2}MW^2 + \frac{1}{2}mw_1^2 \quad (34.2)$$

and eliminating  $w_1$  we find

$$W = 2w_0 \left( 1 + \frac{M}{m} \right)^{-1} \quad (34.3)$$

Therefore, the ratio of the kinetic energy given to the heavy sphere to the original kinetic energy of the light sphere is

$$\frac{\frac{1}{2}MW^2}{\frac{1}{2}mw_0^2} = \frac{4}{\left( 1 + \frac{m}{M} \right)^2} \frac{m}{M} \quad (34.4)$$

If  $m < M$ , this is small compared to unity. If  $m = M$ , the ratio is unity; all the energy is

expected if the molecular weight of the wall (or wire) and the gas are about equal. The results in Table IX, from Eucken and Krome, bear this out (platinum ribbon, 0°C). Roberts<sup>7</sup> discovered that the accommodation coefficient is strongly affected by the presence of a monomolecular film of adsorbed gas on the surface of the wire. For example, the accommodation coefficient for He on tungsten at room temperature is found to be 0.19; after flashing the wire shortly at 2,000°C, the value is reduced to 0.057 and goes then slowly up

TABLE IX  
ACCOMMODATION COEFFICIENTS ON PLATINUM

Xe	Kr	A	Ne	CO	N <sub>2</sub>	H <sub>2</sub>
1	0.94	0.91	0.72	0.84	0.81	0.34

again to the former value, probably due to chemisorption of traces of hydrogen. Neon has, on a clean tungsten wire, an accommodation coefficient of 0.06; with an adsorbed H<sub>2</sub> film, the value is 0.16, with an adsorbed O<sub>2</sub> film, 0.36.<sup>8</sup> It is understandable that an adsorbed gas film increases the accommodation coefficient in the present case, as the He atoms now collide directly with the light molecules of the gas film instead of colliding with the heavy tungsten atoms.

Other measurements have been made by Mann<sup>8a</sup> (Pt surfaces at high temperatures), Blodgett and Langmuir<sup>9</sup> (W), Michels<sup>10</sup> (W) and Raines<sup>11</sup> (Ni) (about 0.07 for He on gas free Ni at room temperature). The accommodation coefficient generally increases with temperature. Roberts gives for He on W, 0.025 at 79°K, 0.057 for 295°K. It is probable that even these low values are too high, as the surface of the wire is probably rough—particularly after heat

transferred in a head on collision of equal billiard balls. If the ratio of the masses is inversed, the heavy sphere striking, we get the same results as if the heavy sphere had been at rest.

If the molecule  $M$  is bound to (or in) a crystal, the question arises whether the masses to which  $M$  is bound, should also be taken into account. For example, if an oxygen atom is adsorbed to a tungsten surface, is  $M$  the mass of O or of  $W + O$ ? This depends on the binding forces, which in turn determine the period of oscillation of the bound particle against the rest of the crystal. If the period is long compared to the collision times,  $M$  is only the mass of the particle hit directly. Otherwise,  $M$  is larger and may be much larger.

<sup>7</sup> *Op. cit.*, *Proc. Roy. Soc.*, A, 129, 146 (1930); 135, 192 (1932); 152, 445 (1935); A. B. van Cleave, *Trans. Faraday Soc.*, 34, 1174 (1938), for adsorbed N<sub>2</sub> and O<sub>2</sub>.

<sup>8</sup> This might have practical consequences. A wire, electrically heated in a gas at low pressure, might be in a stationary state, Joule heat being conducted away by the gas. A slight increase in current might raise the temperature sufficiently to drive the adsorbed gas film off, the effective heat conductivity drops and the wire burns through. See, e.g., H. Busch, *Ann. Physik*, 64, 401 (1921).

<sup>8a</sup> *Proc. Roy. Soc.*, A, 146, 766 (1934); W. B. Mann and W. C. Newell, *ibid.*, A, 158, 397 (1937).

<sup>9</sup> *Phys. Rev.*, 40, 78 (1932).

<sup>10</sup> *Ibid.*, 40, 472 (1932); 44, 604 (1933).

<sup>11</sup> *Ibid.*, 56, 691 (1939).

treatment—and therefore larger than assumed. Michels<sup>10</sup> used electron emission measurements to estimate this effect; similarly, the presence of the adsorbed film can be detected.

A quantitative theory has been developed mainly by Lennard-Jones and Devonshire<sup>12</sup> and their collaborators, basing their calculations on older work.<sup>13</sup> To develop a quantum mechanical theory, an energy of interaction between the particles of the wall and the incoming molecule has to be assumed. The potential energy  $\epsilon$  depends only on the distance  $z$  between the gas molecule and the wall particle ( $z$  normal to the wall). The wall particles vibrate, and it is this vibration which provides the energy to be transferred to the gas molecule. But the amplitude  $z_1$  of this vibration is very small and  $\epsilon$  therefore can be developed into a Taylor series according to  $z_1$ . If we call the momentary distance between the gas molecule and the position of equilibrium of the wall molecule  $z_2$ , we have

$$z = z_2 - z_1 \quad (34.5)$$

$$\epsilon(z) = \epsilon(z_2) + \left( \frac{d\epsilon}{dz} \right)_{z_2} z_1 + \dots \quad (34.6)$$

this being a Taylor development of  $\epsilon$  around  $z_2$ , broken off at the linear term in  $z_1$ . The term  $\epsilon(z_2)$  which does not contain the vibration does not directly affect the transfer of energy between vibration  $z_1$  and motion of the gas molecule ( $z_2$ ), but the second term does.

For the calculation, we can just as well treat the transfer of kinetic energy to the wall vibrations as the reverse. We then have the following situation. On the one hand, we have the crystal which is traversed by longitudinal and transverse waves of a great variety of wavelengths and directions, into which the totality of vibrations of the wall particles can be resolved. On the other hand, we have the gas molecules, coming from a large distance with a given velocity, approaching the wall. When they get near the wall, they get a positive or negative acceleration (mainly defined by  $\epsilon(z_2)$ , compared to which the second term in  $\epsilon$  is small). They rebound and go finally out again with a constant velocity. During their nearness to the wall, they have interacted with the vibrations with an energy  $z_1(d\epsilon/dz)_{z_2}$ . What energy have they lost to the wall?

In this form the problem is of the same mathematical form as that of calculating the amount of radiation a charge accelerated by the interaction  $\epsilon(z_2)$  would emit into the "ether," the crystal behaving like the "ether" (apart from the possibility of longitudinal vibrations). The problem is attacked by calculating the probability that the molecule, whose behavior is described by a wave function determined by the form of  $\epsilon$ , sends a quantum into a particular accoustical wave in the crystal. Then integration over all possible waves which can

<sup>12</sup> A. F. Devonshire, *Proc. Roy. Soc., A*, **158**, 269 (1937); C. Strachan, *ibid.*, **158**, 591 (1937); J. E. Lennard-Jones and C. Strachan, *ibid.*, **150**, 442 (1935).

<sup>13</sup> C. Zener, *Phys. Rev.*, **37**, 556 (1931); **40**, 178, 335, 1016 (1932); J. M. Jackson and N. Mott, *Proc. Roy. Soc., A*, **137**, 703 (1932); J. M. Jackson and A. Howarth, *ibid.*, **142**, 447 (1933).

accept a quantum, and over all molecular velocities according to Maxwell's distribution is effected. The final formula is so complicated that only numerical evaluation is possible. The authors are able, with a "Morse function" for  $\epsilon$ , to use such constants that not only the absolute value but also the temperature dependence of the accommodation coefficient can be fitted, but with the present accuracy it is not possible to do so uniquely (Fig. 27).

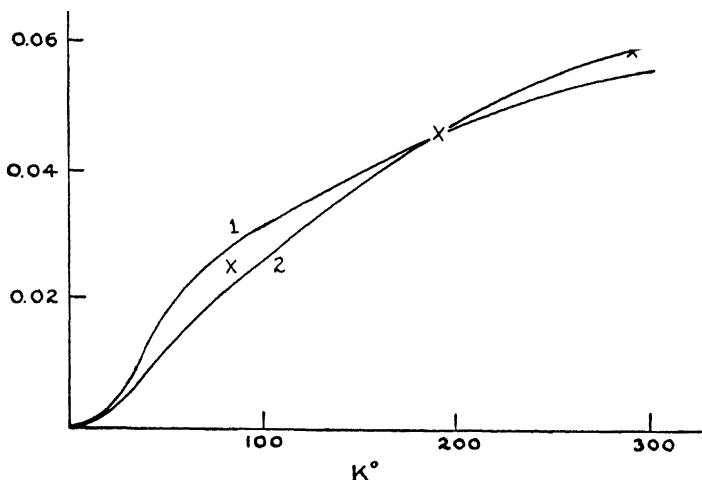


Fig. 27. Theoretical Accommodation Coefficient of He on Tungsten. Experimental Points X, Theoretical Curve 1 with Morse Potential, 2 with Repulsion Only.

For the problem of accommodation of rotational energy an experiment of Rowley and Bonhoeffer<sup>14</sup> is significant. They measured the accommodation on platinum, which had been freed from adsorbed gases by previous heating to 800°C. At 109°K the accommodation coefficient of parahydrogen was found to be 0.365. At that temperature, parahydrogen, in which only the even rotational states are allowed, has no rotational energy left. For normal hydrogen, which at that temperature still has rotational energy in its ortho-component ( $J = 1$ ), the overall  $f'$  is lower, and since the translational part ought to be the same for para- and ortho-hydrogen, a lower  $f'$  for rotation is calculated; at 140°K,  $f'$  for translation 0.43, for rotation 0.26.

As far as vibrational energy is concerned, two cases must again be distinguished. For those molecules which are not adsorbed but bound off immediately after collision, the time of contact is so small that an appreciable adjustment of the internal energy is not to be expected. In agreement with this argument, Whaley,<sup>15</sup> working with wire temperatures between 800°C and 1200°C, where adsorption is negligible, explained his results by assuming complete accommodation for translation and rotation and none for vibration.

<sup>14</sup> *Z. physik. Chem.*, B, 21, 84 (1933).

<sup>15</sup> *J. Chem. Phys.*, 1, 186 (1933); see also P. Doty, *ibid.*, 11, 557 (1943).

Theoretically,<sup>16</sup> this slowness of exchange between vibrations of the molecule and the vibrations of the particles in the solid wall can be understood as due to the low value of the frequencies in the solid compared to those in the adsorbed molecule. To excite a molecular vibration by giving it one quantum, several quanta of the crystal vibrations must be adsorbed simultaneously, a process which is always slow according to quantum theory, if the energy of interaction is not too high (counter example: shower formation in cosmic rays).

For the molecules which are adsorbed, Eucken<sup>17</sup> has developed the following theory. Call  $\tau'$  the average "relaxation time" necessary for the exchange of vibrational energy between solid and gas molecule ( $\tau'$  is similar to the quantity so designated in Section 20), and  $\tau_a$  the average lifetime on the wall of an adsorbed atom. The accommodation coefficient for vibrational energy,  $f_v'$ , is given by

$$f_v' = \tau_a / (\tau_a + \tau') \quad (34.7)$$

This equation should be applicable to the data given in Fig. 27, in the case of most of the gases having more than one atom in the molecule.

Eucken and Bertram<sup>18</sup> found for a number of gases against NiO rather good accommodation (1 to 0.8) but the temperature of their wire was rather low (highest 106°C) so that there was probably strong adsorption. Temperature coefficients of  $1 - f$  have been determined by Eucken and Bertram, Eucken and Krome (*loc. cit.*) and others.<sup>19</sup>

It follows from Eucken and Bertram's measurements together with other data, that  $\tau_a$ , the life time of the adsorbed molecule, diminishes faster with increasing temperature than  $\tau'$ , the time needed for energy exchange. This means that the heat of adsorption is larger than the heat of activation for the exchange. Therefore, with increasing temperature, the "collision" case is approached.

**(35) Thermal Effusion:** The phenomenon of thermal effusion was predicted by Neumann<sup>1</sup> from a theoretical discussion. Feddersen<sup>2</sup> confirmed the predictions experimentally by showing that if two vessels are connected by a tube in which is placed a porous plug and if one end of the porous plug is warmed a pressure difference is developed between the two vessels, the higher pressure appearing at the warm end. Violle,<sup>3</sup> however, raised against these experiments the objection that the results were invalidated by the presence of water vapor.

Reynolds<sup>4</sup> discovered the phenomenon independently of Feddersen, inves-

<sup>16</sup> K. F. Herzfeld and M. Goeppert Mayer, *Z. physik. Chem.*, Bodenstein Festband, 669 (1931).

<sup>17</sup> *Naturwissenschaften*, 25, 209 (1937).

<sup>18</sup> *Z. physik. Chem.*, B, 31, 361 (1936).

<sup>19</sup> W. Hunsmann, *Z. Elektrochem.*, 44, 606 (1938); O. Beeck, *J. Chem. Phys.*, 4, 680, 743 (1936); 5, 268 (1937); C. T. Archer, *Phil. Mag.*, 19, 901 (1935); H. C. Gregory and E. H. Dock, *ibid.*, 25, 129 (1937).

<sup>1</sup> *Ber. d. sächs. Akad. d. Wiss.*, 24, 49 (1872).

<sup>2</sup> *Pogg. Ann.*, 148, 308 (1873).

<sup>3</sup> *J. Phys.*, 4, 97 (1875).

<sup>4</sup> *Loc. cit.*

tigated it experimentally and was able to explain it on the grounds of the kinetic theory. Maxwell <sup>5</sup> has also considered the question and his general formula for the flow of a gas through a tube contains a term which depends on temperature gradients.

The theory is quite simple for the case of a tube whose diameter is small in comparison with the mean free path. The general equation (27.14) is then valid and at the steady state, when there is no flow, the left hand side equals zero, whence

$$\frac{p_2}{p_1} = \frac{\sqrt{T_2}}{T_1} \quad (35.1)$$

Here the conditions are actually present which are described by the approximate calculation for large vessels (Section 31).

Nothing which is dependent on the form or nature of the connecting tube between the two vessels appears in the equation. The only condition that is demanded is that the diameter of the connecting tube be small in comparison with the mean free path. More recently Knudsen <sup>6</sup> has repeated the experiments, obtaining good agreement with the theory. Two vessels were connected through a sufficiently small tube or through a porous diaphragm. One of these vessels was heated, whereupon the pressure in that vessel increased. This increase can be caused by two different processes depending on the conditions of the experiment. If one of the vessels is heated throughout up to the mouth of the capillary, gas *leaves* the heated vessel and the density in the vessel decreases because the pressure increases less than the temperature.

$$c_2 = \frac{p_2}{RT_2} \quad c_1 = \frac{T_1}{T_2} \quad (35.2)$$

If, however, only the mouth of the capillary is heated just at the point where it enters vessel 2, the gas *enters* the latter vessel because it must then exert the same pressure  $p_2$  as in the heated part of the capillary throughout the entire vessel 2 without a change occurring in the temperature in vessel 2.

The flow of a gas in moles through tubes whose diameters are large in comparison with the mean free path may be approximately calculated, for the case in which there is no pressure gradient, as has been shown by Maxwell. There pass from left to right, through the cross-section  $\pi d^2/4$ ,

$$\frac{\pi d^2}{4} N_A \frac{c_1 w_1}{4} = \frac{\pi d^2}{4} \cdot \frac{N_A}{4} \left( cw - \Lambda \frac{\partial cw}{\partial x} \right) \quad (35.3)$$

molecules which come from the distance  $\Lambda$ . Similarly, there come from right to left

$$\frac{\pi d^2}{4} \frac{N_A}{4} \left( cw + \Lambda \frac{\partial cw}{\partial x} \right) \quad (35.4)$$

<sup>5</sup> *Loc. cit.*

<sup>6</sup> *Ann. Physik*, **31**, 205, 633 (1910).

The excess flow from right to left is therefore

$$\frac{\pi d^2}{4} \frac{N_A}{4} 2\Lambda \frac{\partial cw}{\partial x} \quad (35.5)$$

Since there is no pressure gradient,  $p$  is constant throughout, and  $cw^2$  is everywhere constant. Therefore

$$\begin{aligned} \frac{\partial}{\partial x}(cw) &= \frac{\partial}{\partial x} \left( \frac{cw^2}{w} \right) = cw^2 \frac{\partial}{\partial x} \cdot \frac{1}{w} = -cw \frac{1}{w} \frac{\partial w}{\partial x} = -cw \frac{\partial \ln w}{\partial x} \\ &= -\frac{cw}{2} \frac{\partial \ln T}{\partial x} \end{aligned} \quad (35.6)$$

The stream of molecules going from right to left is then given by

$$\frac{\pi d^2}{4} \frac{N_A}{4} 2\Lambda \left( -\frac{cw}{2} \frac{\partial \ln T}{\partial x} \right) = -\frac{\pi d^2}{4} \frac{M}{4m} cw\Lambda \frac{1}{T} \frac{\partial T}{\partial x} = -\frac{\pi d^2}{4} \frac{3}{4m} \eta \frac{1}{T} \frac{\partial T}{\partial x} \quad (35.7)$$

or, expressed in moles, and taken from left to right,

$$+ \frac{\pi d^2}{4} \frac{3}{4M} \eta \frac{1}{T} \frac{\partial T}{\partial x} \quad (35.8)$$

The temperature gradient therefore produces a flow such that gas flows *up* the gradient.

Upon adding this term (35.8) to the right hand side of the equation of flow (27.13) there is obtained an expression for the flow in the most general case involving both temperature and pressure changes. The pressure gradient in the stationary state (zero flow) can then be obtained by setting the left hand side equal to zero. Then for  $d > \Lambda$

$$\frac{dp}{dT} = \frac{6\eta^2 R}{Mp} \frac{1}{\frac{d^2}{4} + 4 \frac{\eta}{\eta_e} \frac{2}{d}} \quad (35.9)$$

In a tube closed at each end the total gas flow produced by the pressure gradient is, on the average, compensated by the flow produced by the temperature gradient. This, however, cannot be the case at each point in the cross-section of the tube because the Poiseuille flow is greater at the middle of the tube than near to the periphery. Therefore, at the center of the tube, the action of the pressure gradient will dominate and, at the rim, the action of the temperature gradient. Since the total flow is zero there will be a flow along the walls toward the higher temperature and another at the center toward the lower.<sup>7</sup>

<sup>7</sup> This can be deduced quantitatively in the following manner. The total thermal flow (35.8) is compensated by the average Poiseuille flow  $\bar{W}$  (cf. Equation [27.18]) times the cross-section  $\pi d^2/4$ . At any distance  $r$  from the axis, the flow per unit area is given as: resultant

For high pressures Equation (35.9) may be integrated (neglecting  $\eta/\eta_e$  and setting  $\eta \sim \sqrt{T}$ ) with the result

$$p_2^2 - p_1^2 = \frac{6\eta_0^2}{d^2} \frac{R}{T_0} \overline{M} (T_2^2 - T_1^2) \quad (35.11)$$

Knudsen <sup>8</sup> has tested this formula (taking into account the dependence of  $\Lambda$  upon the temperature) and has found that the best agreement is obtained <sup>9</sup> with the factor 7.4 instead of 6. In one experiment ten tubes 5 cm long and 0.374 mm in diameter were connected to each other through wide tubes, so that the pressure differences were added as are the potential differences of galvanic elements connected in series. The left end of each capillary was heated electrically to about 380°C, and the right end of each maintained at about 50°C. Hydrogen at atmospheric pressure in this apparatus gave a total pressure difference of 0.039 mm of mercury (calc. 0.034). At an average pressure of 6.69 mm the pressure difference was 1.93 (calc. 2.04). More recently Knudsen <sup>10</sup> has extended Equation (35.9) to the pressure region throughout which the mean free path is of the same order of magnitude as the radius of the tube, and has checked his deductions experimentally.

The formulas treated above are of great practical importance in the measurement of the pressure in a vessel by means of a manometer which is at a different temperature.<sup>11</sup> Except for high pressures, the pressure read at the manometer will not be the true pressure in the vessel. The correction is easy to make only in two extreme cases. The simpler case is present if the diameter of the tubes connecting the vessel with the manometer is everywhere small compared with the mean free path. In this case the distribution of the temperature along the tube does not matter, but only the temperature at the two ends; Equation (35.1) can then be used directly. The other extreme case requires that the mean free path be small throughout when compared with the diameter of the vessel. In this case Equation (35.9) must be used. If the diameter of the tube is uniform, the distribution of temperatures is again of no importance. Even then the application of this equation to experimental data involving large temperature intervals is attended by mathematical difficulties since in this case the dependency of  $\eta$  upon  $T$  and of  $\eta/\eta_e$  upon  $p$  and  $T$  must be taken into account. A graphical method of integration has been used by Wilson.<sup>12</sup>

flow  $W$  equal thermal flow minus Poiseuille flow, or

$$W = \frac{3}{4M} \eta \frac{1}{T} \frac{dT}{dx} \left( 2 \frac{4r^2}{d^2} - 1 \right) \quad (35.10)$$

<sup>8</sup> *Ann. Physik*, **33**, 1435 (1910).

<sup>9</sup> It should be noted that in (35.9) and subsequently the factor 1/3 has been used in the expression for  $\eta$  (see Equation [21.5]). If this is replaced by 0.499 (cf. Equation [21.10]), the number 6 in (35.9) and (35.10) should be replaced by 4.

<sup>10</sup> *Ibid.*, **83**, 797 (1927).

<sup>11</sup> P. H. Emmett and J. F. Shultz, *J. Am. Chem. Soc.*, **55**, 1367 (1933); F. C. Tompkins and D. E. Wheeler, *Trans. Faraday Soc.*, **29**, 1248 (1933).

<sup>12</sup> F. R. Bichowsky and C. W. Wilson, *Phys. Rev.*, **33**, 851 (1929).



In Wilson's case, a vessel containing He at about 1500°K was connected by an 8 mm tube to a manometer at room temperature. If a pressure of 0.389 mm was read on this manometer, Equation (35.2) would give a pressure in the vessel of 0.496. The exact calculation by the graphical method gives 0.566, and the experiment (rate of flow through small opening) 0.572.

Knudsen deduced a somewhat more complicated formula in which the factor 6.1 takes the place of 4 in the coefficient of the slip. The entire expression is preceded by a somewhat smaller coefficient and the change in  $\Lambda$  with the temperature according to Sutherland (Section 13) is taken into account.

A very detailed study of the pressure difference for the whole range  $0 \leq d/\Lambda \leq \infty$  has been undertaken by S. Weber,<sup>13</sup> who developed a rather complicated formula which agrees well with his measurements. He considered<sup>14</sup> also the case where the helium thermometer is used to measure temperatures in the region of liquid helium. He measured, at room temperature, the pressure in the manometer whose bulb is in the liquid He bath. In the bulb, the density was so high that  $d/\Lambda \sim \infty$ ; at room temperature in the connected manometer  $\Lambda > d$ . Weber found (2 room temperature, 1 bulb)

$$\left(\frac{p_2}{p_1}\right)^{1+4/n} = \text{const} \times p_1 \left(\frac{T_2}{T_1}\right)^{2\mu/n} \quad (35.12)$$

where  $n$  appears in the exponent (cf. [21.11], [21.12])

$$\frac{\eta_2}{\eta_1} = \left(\frac{T_2}{T_1}\right)^{\frac{1}{2} + \frac{2}{n}} \quad (35.13)$$

$$\text{and} \quad \mu = 1.25 - \frac{0.25}{1 + k \frac{d}{\Lambda}} \quad (35.14)$$

If the ends of a capillary along which a temperature gradient exists are connected by means of a wide glass tube, a steady current of gas may be maintained by heating one end of the capillary. This is somewhat analogous to thermoelectric currents.

There is also the converse effect. Dufour<sup>15</sup> has found that upon diffusion through a porous plate (for example, of hydrogen into a vessel containing air) the temperature at the inlet side is raised.

Knudsen<sup>16</sup> has repeated these experiments also. Upon streaming air through a glass tube in which was placed a plug of glass wool he found a temperature increase at the inlet end. With hydrogen at an inlet pressure of 2.6 mm and a pressure difference of 2.54 mm, this amounted to about 0.06° and

<sup>13</sup> *Comm. Univ. Leiden, Suppl.*, 71b, 11 (1933); S. Weber and W. H. Keesom, *Comm. Univ. Leiden*, 223b, 9 (1933); S. Weber, W. H. Keesom, and G. Schmidt, *ibid.*, 246a (1938); S. Weber, *ibid.*, 246b (1938); S. Weber and G. Schmidt, *ibid.*, 246c (1938).

<sup>14</sup> S. Weber, *ibid.*, 246d (1938).

<sup>15</sup> *Arch. de sci. phys. et nat. Genf.*, 45, 9 (1872); *Pogg. Ann.*, 148, 490 (1873).

<sup>16</sup> Congress Solvay 1911.

at the inlet pressure of 171 mm and a pressure difference of 11 mm, to about  $0.62^\circ$ . At the outlet the gas has returned to its initial temperature wherefore Knudsen concludes that the effect is not due to a Joule-Thomson heating. In contradiction to this last statement Dufour has found a temperature drop in the space into which the hydrogen left the capillary (see also section 52).

Weber<sup>17</sup> has ascribed this phenomenon to the fact that in the Poiseuille flow of a gas each molecule carries, on the average, an energy equal to  $\frac{5}{2}kT$ . In the uniform flow of a gas, the distribution formula is

$$dN = N_0 \left( \frac{m}{2\pi kT} \right)^{\frac{3}{2}} e^{-\frac{m}{2kT}[(\xi - \xi_0)^2 + \eta^2 + \zeta^2]} d\xi d\eta d\zeta \quad (35.15)$$

The average energy transported per molecule, passing through 1 sq cm per sec is

$$\left. \begin{aligned} \bar{\epsilon} &= \frac{\int_{-\infty}^{+\infty} \frac{1}{2} m (\xi^2 + \eta^2 + \zeta^2) \xi dN}{\int_{-\infty}^{+\infty} \xi dN} \\ &= \frac{\frac{1}{2} m \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \xi (\xi^2 + \eta^2 + \zeta^2) e^{-\frac{m}{2kT}[(\xi - \xi_0)^2 + \eta^2 + \zeta^2]} d\xi d\eta d\zeta}{\int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \xi e^{-\frac{m}{2kT}[(\xi - \xi_0)^2 + \eta^2 + \zeta^2]} d\xi d\eta d\zeta} \\ &= \frac{5}{2} kT \end{aligned} \right\} \quad (35.16)$$

In the evaluation of this integral all terms containing powers of  $\xi_0$  higher than the first are neglected since  $\xi_0 \ll \xi$ .

The  $\frac{5}{2}kT$  is composed of thermal kinetic energy ( $\frac{3}{2}kT$ ) and mechanical energy ( $p v / N = kT$ ). If the conditions of molecular flow obtain, the average energy carried per molecule is only  $\frac{4}{2}kT$ , as then the distribution is undisturbed, and the energy transport is given by

$$\left. \begin{aligned} \bar{\epsilon} &= \frac{\int \frac{1}{2} m (\xi^2 + \eta^2 + \zeta^2) \xi dN'}{\int \xi dN'} \\ &= \frac{\frac{1}{2} m \int_0^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \xi (\xi^2 + \eta^2 + \zeta^2) e^{-\frac{m}{2kT}(\xi^2 + \eta^2 + \zeta^2)} d\xi d\eta d\zeta}{\int_0^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \xi e^{-\frac{m}{2kT}(\xi^2 + \eta^2 + \zeta^2)} d\xi d\eta d\zeta} \\ &= \frac{4}{2} kT \end{aligned} \right\} \quad (35.17)$$

$$dN' = N_0 \left( \frac{m}{2\pi kT} \right)^{\frac{3}{2}} e^{-\frac{m}{2kT}(\xi^2 + \eta^2 + \zeta^2)} d\xi d\eta d\zeta \quad (35.18)$$

<sup>17</sup> Z. Physik, 24, 267 (1924).

That it is larger than  $\frac{3}{2}kT$  in both cases, comes from the fact that the molecules with more energy travel faster. The integration with respect to  $\xi$  is carried from  $-\infty$  to  $\infty$  in Equation (35.16) and from 0 to  $\infty$  in Equation (35.17) because in the former case the distribution function is modified to account for the one sided flow with a constant  $N_0$ , while in the latter case it does not, but the flow is determined by the variation of  $N_0$  with  $x$ . To give the distribution in the case of molecular flow, one ought to say that at any place the distribution is made up by  $N_-$  molecules with a  $\xi$  between 0 and  $\infty$  going from left to right and  $N_+$  molecules with  $\xi$  between 0 and  $-\infty$  going from right to left.

From the foregoing discussion it follows that at a point at which the flow changes from Poiseuille to molecular, energy is lost by the gas and must appear as heat in the surroundings. Such a transition in the type of flow is caused by the presence of the porous plug. Conversely, the outlet end of the plug gets colder. The difference for the two types of flow may be ascribed to the fact that there is no mass motion of the gas in its molecular flow.

**(36) Equilibrium of Gas-filled Tubes with Temperature Gradients. Stress on a Wall with Temperature Gradient Parallel to it:** Consider a straight cylindrical closed tube filled with gas, suspended horizontally. Assume one end of the tube is heated and the other end is cooled, so that a stationary, uniform temperature gradient is established along the tube. It is clear from mechanical principles that no resultant force, which would deflect the tube as a whole, acts on the solid material of the tube walls. But, if the diameter of the tube is not infinitely large compared to the mean free path, the pressure acting on the cap at the hot end of the tube is higher than that acting at the cold end. The excess pressure would move the tube toward the hotter side. This force must be compensated by an effect of the gas on the walls of the tube, which has the character of a shearing stress ( $p_{12}$  dynes/cm<sup>2</sup>) exerted parallel to the wall toward the colder end.

We shall consider a short piece of the tube of length  $dx$ . The pressure difference,  $(\partial p/\partial x)dx$ , over the distance  $dx$ , acting on the area  $\pi(d^2/4)$  must be taken up by the stress  $p_{12}$ , acting on the cylinder mantle of area  $dx \cdot \pi d$ , so that

$$p_{12} = -\frac{d}{4} \frac{\partial p}{\partial x} \quad (36.1)$$

Take now first the case of low densities,  $\Lambda > d$ . Equation (35.1) can be written

$$\frac{\partial p}{\partial x} = \frac{1}{2} \frac{p}{T} \frac{\partial T}{\partial x} \quad (36.2)$$

and from (36.1) and (36.2),

$$p_{12} = -\frac{d}{8} \frac{p}{T} \cdot \frac{\partial T}{\partial x} \quad (36.3)$$

The negative sign indicates that the stress has a direction opposite to that of the gradient, i.e., is directed toward lower temperatures. This stress arises

from the fact that an element of the wall is hit a harder blow by a molecule coming from the high temperature side than by one coming from the low temperature side, although their number is equal (no flow).

For intermediate pressures we have, using (35.9) but neglecting the slip term in the denominator,

$$\frac{\partial p}{\partial x} = \frac{24\eta^2 R}{Mpd^2} \frac{\partial T}{\partial x} \quad (36.4)$$

or

$$p_{12} = - \frac{6\eta^2 R}{Mpd} \frac{\partial T}{\partial x} \quad (36.5)$$

Knudsen<sup>1</sup> has calculated the stresses directly from the collision of the molecules with the wall.

Similar stresses and flow phenomena parallel to a wall, along which a temperature gradient exists, play a decisive role in the radiometer effect at moderate pressures (Section 40).

### (37) The Movement of Small Particles in a Temperature Gradient:

Tyndall<sup>1</sup> observed that a heated body is surrounded, in dusty air, by a dark (dust-free) space. The effect was confirmed by Lord Rayleigh,<sup>2</sup> Lodge,<sup>3</sup> and particularly Aitken,<sup>4</sup> who saw that the dust particles moved along the temperature gradient toward lower temperatures. Later observations were made by Tolman<sup>5</sup> and Watson.<sup>6</sup> An elementary theory was given by Cawood.<sup>7</sup> The following treatment for small particles follows arguments of Einstein.<sup>8</sup>

In this section, the theory will be given for particles small compared to  $\Lambda$ . In this case, the distribution of gas molecules in the temperature gradient is the same as if the particle were not present (see analogous considerations in Section 29). We take as direction of the gradient the  $z$ -axis, and allow for the deviation from the Maxwell distribution. The distribution in the present case is given by Equations (16.4), (16.5) and (16.9), with no bulk flow of the gas ( $W = 0$ , Equation [16.2]) and a temperature gradient in the  $z$ -direction only.

For  $\Phi_1$  we use the first two terms of a development into powers of  $mw^2/2kT$ ,

$$\Phi_1 = a + b \frac{mw^2}{2kT} \quad (37.1)$$

<sup>1</sup> *Ann. Physik*, **31**, 205 (1910); **33**, 1435 (1910).

<sup>2</sup> *Proc. Roy. Inst.*, **6**, 3 (1870).

<sup>3</sup> *Proc. Roy. Soc.*, **34**, 414 (1882).

<sup>4</sup> *Nature*, **28**, 297 (1883); O. Lodge and Clark, *Proc. Phys. Soc.*, **6**, 1 (1884).

<sup>5</sup> *Trans. Roy. Soc. Edinburgh*, **32**, 239 (1884).

<sup>6</sup> *J. Phys. Chem.*, **24**, 421 (1920).

<sup>7</sup> *Trans. Faraday Soc.*, **32**, 1073 (1936).

<sup>8</sup> *Ibid.*, **32**, 1068 (1936).

<sup>9</sup> *Z. Physik*, **27**, 1 (1924); see also A. Rubinowicz, *Ann. Physik*, **62**, 691 (1920).

so that the distribution function takes the form

$$dN = N_0 \left( \frac{m}{2\pi kT} \right)^{\frac{3}{2}} \times e^{-\frac{mw^2}{2kT}} \left[ 1 - \zeta \left( \frac{m}{2kT} \right)^{\frac{1}{2}} \frac{1}{T} \frac{\partial T}{\partial z} \Lambda \left( a + b \frac{mw^2}{2kT} \right) \right] d\xi d\eta d\zeta \quad (37.2)$$

We next express  $a$  and  $b$  by quantities which can be measured directly. The absence of mass flow in the  $z$ -direction, expressed by

$$\int \zeta dN = 0 \quad (37.3)$$

leads to

$$b = -\frac{2}{3}a \quad (37.4)$$

The kinetic energy of translation, transported by the molecules in the  $z$ -direction, is

$$\int \frac{1}{2}mw^2\zeta dN = + N_0kT \left( \frac{kT}{2m} \right)^{\frac{1}{2}} \Lambda a \frac{1}{T} \frac{\partial T}{\partial z} \quad (37.5)$$

This energy flow can also be expressed according to (31.10) as

$$- 2.5 \times \frac{3}{2} \frac{R}{M} \eta \frac{\partial T}{\partial z} \quad (37.6)$$

so that

$$N_0\Lambda ak = -\frac{15}{4} \left( \frac{2m}{kT} \right)^{\frac{1}{2}} \frac{R}{M} \eta \quad (37.7)$$

Consider a surface element  $dS$ . Let  $\vartheta$  be the angle between the normal of  $dS$  and the  $z$ -direction. Introduce a new "local" coordinate system  $X', Y', Z'$ , with  $Z'$  parallel to the normal on  $dS$ . The number of molecules falling in unit time on  $dS$  is  $\zeta' dN dS$ . We assume that the molecules impinging on  $dS$  are adsorbed and reevaporate, after the Brownian motion of rotation has destroyed any connection between the orientations of the particle at the time of adsorption and at the time of evaporation. Therefore, the evaporating molecules transfer, on the average, no linear momentum to the particle. Each impinging molecule transfers to the particle a linear momentum in the  $z$ -direction (upon adsorption) of  $m\zeta$ . The linear momentum in the other directions average out for the whole particle.

The total momentum in the  $z$ -direction transferred per second to  $dS$  is

$$dM_z' = dS \int m\zeta\zeta' dN \quad (37.8)$$

with  $dN$  given by (37.2).

The result <sup>9</sup> of the integration is that the part  $dM_z$  of the linear momentum in the  $z$ -direction, transferred to  $dS$  per second, which is due to the temperature gradient is given by (37.14). Thus,

$$dM_z = -dS(1 + \cos^2 \vartheta) \frac{3}{4} \frac{R}{M} \eta \left( \frac{M}{2\pi RT} \right)^{\frac{1}{2}} \frac{\partial T}{\partial z} \quad (37.14)$$

Or, integrated over the surface,

$$M_z = -\frac{3}{4} \left( \frac{M}{2\pi RT} \right)^{\frac{1}{2}} \eta \frac{\partial T}{\partial z} \int dS(1 + \cos^2 \vartheta) \quad (37.15)$$

This quantity is independent of the pressure.

If (37.15) is compared with Equation (29.8), which gives the resisting force acting on a particle small compared to  $\Lambda$ , which moves through the gas with a speed  $W$ , it is seen that both depend on size and shape in the same way, namely through the last integral in (37.12). The speed which the particle takes due to the temperature gradient is, therefore,

$$W = -\frac{3}{4} \frac{R}{M} \frac{\eta}{p} \frac{\partial T}{\partial z} \quad (37.16)$$

and this is independent of size and shape of the particle, provided it is small compared with the mean free path. The particle moves along the temperature gradient toward lower temperatures (negative sign!).

<sup>9</sup> The procedure is as follows: Introduce angles  $\vartheta'$ ,  $\varphi'$  which define the orientation of the molecular velocity  $w$  with respect to the normal of  $dS$ . Then in (37.2),

$$d\xi d\eta d\zeta = d\xi' d\eta' d\zeta' = w^2 dw \sin \vartheta' d\vartheta' d\varphi' \quad (37.9)$$

$$\zeta' = w \cos \vartheta' \quad (37.10)$$

In the integration, the angle  $\vartheta'$  goes from zero to  $\pi/2$ , the angle  $\varphi'$  from zero to  $2\pi$ , since the molecules may come from any direction of the hemisphere above  $dS$ .

Furthermore

$$\zeta = w(\cos \vartheta \cos \vartheta' + \sin \vartheta \sin \vartheta' \sin \varphi') \quad (37.11)$$

This uses a formula of spherical trigonometry for the angle between the direction of  $z$  and of  $w$ . Employing the abbreviation  $y^2 = mw^2/2kT$ , and introducing these quantities into (37.8) it is found that

$$\begin{aligned} dM_z' = dS 2N_0 k T \pi^{-\frac{1}{2}} \int e^{-y^2} y^4 dy \int \cos \vartheta' \sin \vartheta' d\vartheta' d\varphi' \left[ \cos \vartheta \cos \vartheta' + \sin \vartheta \sin \vartheta' \sin \varphi' \right. \\ \left. - \Lambda a \frac{1}{T} \frac{\partial T}{\partial z} y(1 - \frac{2}{3} y^2)(\cos \vartheta \cos \vartheta' + \sin \vartheta \sin \vartheta' \sin \varphi')^2 \right] \end{aligned} \quad (37.12)$$

Upon integrating first with respect to  $y$ , then with respect to  $\varphi'$ , finally with respect to  $\vartheta'$ , the result is (with  $N_0 k T = p$ , the hydrostatic pressure)

$$dM_z' = \frac{1}{2} p dS \cos \vartheta + \frac{1}{2} p dS(1 + \cos^2 \vartheta) \frac{1}{5\sqrt{\pi}} \Lambda a \frac{1}{T} \frac{\partial T}{\partial z} \quad (37.13)$$

The first part is simply the component of the force in the  $z$ -direction due to half the hydrostatic pressure (half, because only the impact was counted) and cancels out when integrated over the whole particle. The second part is called  $dM_z$  in the text and, with (37.7), gives (37.14).

When the particle is larger than the mean free path, the problem has to be treated by the methods which apply to the radiometer forces and are developed in Section 40. The equations for the force exerted on a sphere and the speed attained by it are given as (40.4) and (40.5). In this case, also, the speed is independent of the size (but not the shape) of the particle.

The "Aitken" effect has practical importance (although in most cases the particle size makes Section 40 applicable). If a hot pipe runs parallel to a wall, the dust will accumulate on the wall, while the pipe remains dustfree. Dust can also be removed from a gas by passing the gas through a temperature gradient.<sup>10</sup>

**(38) Radiometer Forces at Low Pressures:** It has been found that solid objects may experience unbalanced forces when surrounded by a gas which is not in thermal equilibrium. Such forces, aside from those caused by convection currents, are known as radiometer forces. The name is due to the fact that in the earlier experiments on the subject the disturbance of the thermal equilibrium (i.e., non-uniform temperature distribution) was produced by radiation. These radiometric forces vary greatly with the gas pressure (see below). Here again the theoretical treatment of the phenomena will be facilitated by considering separately the cases of low and high pressures.<sup>1</sup> As before, the criterion of the magnitude of the pressure is the length of the mean free path. If this is large in comparison with the important dimensions of the apparatus, the pressure is "low" and vice versa. Knudsen<sup>2</sup> has shown that the relations are particularly simple in the case of very low pressures. Two parallel plates are placed opposite each other in a vessel, the walls of which are at the temperature  $T_1$ . One of the plates is maintained at the temperature  $T_1$  and the other at the temperature  $T_2$ . If the mean free path is large in comparison to all the dimensions of importance (distance from the plates to the walls and the distance between the plates) only collisions of the molecules with solid surfaces come into account and the velocity of each molecule is determined by the temperature of the surface from which it comes. Since a stationary state is assumed, the same number of molecules must pass each sq cm in opposite directions throughout, i.e., the number of collisions per second on unit surface must be constant at all points. Let  $N_{Ac}$  be the density of the molecules in the undisturbed gas, that is, in the gas between the plate of temperature  $T_1$  and the outer wall which is at the same temperature. The number of collisions on the plate due to molecules coming from the outer wall is then  $N_{Ac}w_1/6$  and the pressure exerted equals the gas pressure  $p = Mcw_1^2/3$ . Let  $N_{Ac1}$  equal the density of the molecules in the region between the plates which move from

<sup>10</sup> H. H. Watson, *Trans. Faraday Soc.*, **32**, 1037 (1936); S. C. Blacktin, *J. Soc. Chem. Ind.*, **58**, 334 (1939); **59**, 153 (1940).

<sup>1</sup> The treatment of Section 37 assumes that the particle is small compared with  $\Lambda$ , but the vessel as a whole large compared to  $\Lambda$ , so that the velocity distribution valid for heat conduction at intermediate pressures is established in the gas.

<sup>2</sup> *Ann. Physik*, **32**, 809 (1910); **34**, 823 (1911); M. von Smoluchowski, *ibid.*, **34**, 182 (1911); **35**, 983 (1911).

plate 1 to plate 2 with the velocity  $w_1$ , and  $N_{Ac_2}$  be the density of these moving from 2 to 1 with the velocity  $w_2$ . Then the total density between the plates is  $3N_A(c_1 + c_2)$ . Since there are the same number of collisions per second upon unit area of all the surfaces involved

$$c_1 w_1 = c_2 w_2 = \frac{c w_1}{6} \quad (38.1)$$

The pressure exerted <sup>3</sup> on that side of plate 1 which faces plate 2 is

$$\begin{aligned} c_1 M w_1^2 + c_2 M w_2^2 &= c_1 M w_1 (w_1 + w_2) = c M w_1 (w_1 + w_2) \\ c M w_1^2 \left(1 + \frac{w_2}{w_1}\right) &= \frac{p}{2} \left(1 + \sqrt{\frac{T_2}{T_1}}\right) \end{aligned} \quad (38.2)$$

The excess pressure on plate 1 which tends to force it away from plate 2 is therefore <sup>4</sup>

$$P = \frac{p}{2} \left( \sqrt{\frac{T_2}{T_1}} + 1 \right) - p = \frac{p}{2} \left( \sqrt{\frac{T_2}{T_1}} - 1 \right) \quad (38.3)$$

If plate 1 is movable  $P$  can be measured and (38.3) be used to calculate  $p$ , the gas pressure. The measurement is independent of the nature of the gas, being equally applicable to vapors of mercury or those coming from stopcock grease. In this respect this method is preferable to the McLeod gauge. The force  $P$  can be increased by increasing the temperature difference. Plate 2 experiences no unbalanced force since it is confronted on both sides by cold surfaces (plate 1 and wall of the vessel). The reaction (excess pressure) to the force acting on plate 1 is supplied by the wall of the vessel opposite plate 2.

It has so far been assumed that the molecules acquire the temperature of the plate immediately upon collision with the plate. Equation (38.3) is independent of this assumption.<sup>5</sup>

<sup>3</sup> The first term on the left of this equation signifies the pressure exerted by the *recoil* of molecules from plate 1, the second term the pressure due to the *impact* of molecules on plate 1.

<sup>4</sup> This equation had been previously obtained by Reynolds.

<sup>5</sup> Maxwell's assumption that the fraction  $1 - f$  of the molecules is reflected without change in energy and that the fraction  $f$  is emitted at the temperature of the emitting plate leads to the following results: Both the group of molecules moving from 1 to 2 as well as the group of molecules moving from 2 to 1 contain molecules which are at the temperature of plate 2 and molecules which are at the temperature of plate 1. The total number of molecules passing per second through any cross section must equal the number passing in the same time in the opposite direction. Therefore

$$c_1^\dagger w_2 + c_1^\dagger w_1 = c_2^\dagger w_2 + c_1^\dagger w_1 \quad (38.4)$$

The  $N_A c_2^\dagger w_2$  molecules leaving plate 1 per second with the velocity  $w_2$  corresponding to the temperature of plate 2 constitute the reflected fraction  $(1 - f)$  of  $N_A c_1^\dagger w_2$  molecules colliding with plate 1 with this velocity, for the  $N_A c_1^\dagger w_1$  molecules which have already the velocity  $w_1$  corresponding to plate 1 before collision naturally will not change their energy upon collision



It must be emphasized that, at *low* pressures, the radiometer force is always directly proportional to the pressure. The relation between the force and the temperature, however, will vary with the type of apparatus, Equation (38.3) expressing the behavior only of the type for which it was deduced, namely, two parallel plates at different temperatures.

(39) **The Absolute Manometer:** Knudsen has applied the results of the last paragraph to the measurement of low pressures. Since, as pointed out above, the radiometer force is in this case independent of the nature of the gas, the

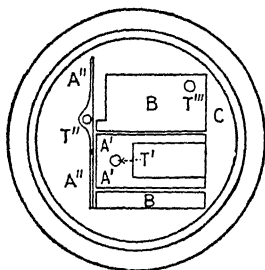


FIG. 28.

instrument is called the "absolute manometer."

It can be used to measure condensable vapors which are not recorded by the McLeod gauge.<sup>1</sup> Knudsen has described several forms of his manometer. Fig. 28 is a plan of a type which is suitable for absolute measurements. A copper cylinder  $A'$ , 1.63 cm in diameter, is set in a glass bell jar which can be evacuated. The bell jar is lined with a blackened metal tube  $C$  in order to promote uniformity of temperature. The polished base of the copper cylinder is heated electrically, thus constituting the hot plate.

The cylinder is provided with the thermometer  $T'$  and, to give a sharp limit to the flow of heat, it is surrounded with a copper block  $B$ , the distance between the two being 0.174 mm. The block  $B$  has the temperature of the surroundings (thermometer  $T''$ ). The action of  $B$  is similar to that of the guard ring of a condenser. A copper plate  $A''$ , provided with the thermometer  $T''$ , is suspended in front of the base of the heated copper cylinder by means of a platinum wire 0.1 mm in diameter. The distance between  $A'$

with plate 1. Hence

$$c_2^{\dagger}w_2 = (1 - f)c_2^{\dagger}w_2 \quad (38.5)$$

Similarly at the upper plate

$$(1 - f)c_1^{\dagger}w_1 = c_1^{\dagger}w_1 \quad (38.6)$$

Substitution in (38.4) gives

$$c_2^{\dagger}w_2 \quad c_1^{\dagger}w_1 \quad \text{and} \quad c_2^{\dagger}w_2 : c_1^{\dagger}w_1 \quad (38.7)$$

Furthermore, the total number of collisions with plate 1 is, as before,

$$c_1^{\dagger}w_1 + c_2^{\dagger}w_2 = cw_1/6 \quad (38.8)$$

Upon substitution of all the various quantities the total excess pressure is seen to have the same value as before,

$$M \left( c_2^{\dagger}w_2^2 + c_1^{\dagger}w_1^2 + c_2^{\dagger}w_2^2 + c_1^{\dagger}w_1^2 - \frac{2cw_1^2}{6} \right) = \frac{p}{2} \left( \sqrt{\frac{T_2}{T_1}} - 1 \right) \quad (38.9)$$

On the other hand a complicated result is obtained from the assumption that each molecule exchanges energy on colliding with the walls, but does not do so completely, or if  $f$  is assumed to depend upon the temperature. (See M. von Smoluchowski, *Ann. Physik*, **34**, 182, 383 (1911); also E. Fredlund, *ibid.*, **13**, 802 (1932); **30**, 99 (1937).)

<sup>1</sup> This must not be confused with the hot wire manometer (Pirani gauge) which measures thermal conductivity (Section 32).

and  $A''$  is 0.12 mm, the effective area 2.1 cm<sup>2</sup> and the distance from the supporting wire to the mid point of the hot plate is 1.2 cm. The angular displacement of the plate is measured at a known temperature difference. With a temperature difference of 46° a pressure of hydrogen equal to 0.002 mm of mercury gives a deflection of a beam of light reflected from a mirror on the moving plate equal to 4 mm. Deviations from the simple formula<sup>2</sup> set in at pressures greater than 0.006 mm. Another type of the instrument which is suited for relative measurements is due to Knudsen.<sup>3</sup>

Gaede<sup>4</sup> has built a manometer by suspending, from a quartz fiber, an aluminum foil stretched on a frame. One wall of the vessel is heated and the deflection by the Knudsen effect measured. If oscillations of the frame are electromagnetically excited and the damping through gas viscosity observed, the molecular weight of the gas can also be determined.

The equations for higher pressure will be treated later.

(40) **Radiometer Forces at High Pressures:** Fresnel<sup>1</sup> was the first to note that bodies suspended in an attenuated gas receded upon irradiation. Crookes<sup>2</sup> investigated this phenomenon and constructed the radiometer which is usually seen as a scientific toy, but which in the improved form, due to Nichols and others,<sup>3</sup> can be used to measure the amount of incident radiant energy. Light metallic vanes are mounted on an axis and the whole placed in an evacuated glass bulb. One side of each of the vanes is polished and the other side is blackened.<sup>4</sup> A quantitative experimental investigation showed Crookes that the force is proportional to the intensity of the incident radiation and dependent upon the gas pressure within the bulb. He had already attempted to explain the phenomenon by saying that the light is more strongly absorbed on the blackened side; this side is therefore warmer and the molecules exert a greater pressure upon it. But, as Crookes himself realized, this explanation is false since it neglects the fact that at high pressures the number of collisions with the hot side is less than the number on the cold side by the factor  $1/\sqrt{T}$ . This just compensates the effect of the increased velocity ( $\propto \sqrt{T}$ ). Schuster<sup>5</sup> found that the surrounding gas has a momentum equal and opposite to that of the vanes so that there is no force acting on the center of gravity of the

<sup>2</sup> According to E. Fredlund, *Ann. Physik*, **13**, 802 (1932), the limit is  $\Lambda$  equal to about 10 $\lambda$ .

<sup>3</sup> *Ibid.*, **44**, 525 (1914).

<sup>4</sup> *Z. tech. Physik*, **15**, 664 (1934). For a more detailed description of the construction and use of the absolute manometer see E. von Angerer, *Ann. Physik*, **41**, 10 (1913); Woodrow, *Phys. Rev.*, **4**, 491 (1914); Shrader and Sherwood, *ibid.*, **12**, 70 (1918); S. Dushman, *Production and Measurement of High Vacuum* (Schenectady, 1922); L. Dunoyer, *Vacuum Practice*, trans. by J. H. Smith (D. Van Nostrand Co., 1928).

<sup>1</sup> *Ann. chim. phys.*, **29**, 57, 107 (1825).

<sup>2</sup> *Phil. Trans. Roy. Soc.*, **164**, 501 (1874); **166**, 340 (1876); **170**, 132 (1880).

<sup>3</sup> E. F. Nichols, *Wied. Ann.*, **60**, 401 (1897); E. Pringsheim, *ibid.*, **18**, 32 (1883). Cf. also W. Donle, *ibid.*, **68**, 306 (1899); B. J. Spence, *J. Opt. Soc. Am.*, **6**, 625 (1922); E. Nichols and J. Tear, *Phys. Rev.*, **21**, 587 (1923); O. Sandrik, *J. Opt. Soc. Am.*, **12**, 355 (1926).

<sup>4</sup> The arrangement is similar to an anemometer, the light taking the place of the wind.

<sup>5</sup> *Phil. Trans. Roy. Soc.*, **166**, 715 (1880).

whole system. Hence, the phenomenon is not due to the pressure of the light.

The theoretical treatment of the problem is rather complicated. Maxwell<sup>6</sup> pointed out that the existence of these forces is bound up with a gas motion tangentially along the surface of the solid. Almost simultaneously with Maxwell, Reynolds<sup>7</sup> attempted to develop the theory of radiometer forces. The noteworthy idea which he added to the problem was that thermal effusion and radiometer forces are evidences of the same phenomenon. If the solid body (tube) is immovable, only the gas is set in motion by the temperature gradient. In radiometers the solid body also may move. He first emphasized that a temperature difference gives no resultant force on infinitely large plates, but that the action takes place at the edges of the vanes due to the divergence of the lines of flow of heat. As in the case of Maxwell's treatment the second differential quotient of the temperature is the determining factor. Reynolds, however, has taken into account the slip at the outset in his formulae by assuming the "length of transport interval" to be different in the vicinity of a solid body and in the interior of the gas. In this manner he arrives at a total force which is different from zero.

The first simple discussion leading to an accurate result was given by A. Einstein.<sup>8</sup> The development is approximate and only attempts to give a qualitative description which will be correct to within the order of magnitude. In order to simplify the problem as much as possible, Einstein limits himself to radiometric forces produced by a flow of heat rather than light. He considers a linear homogeneous flow of heat to be established in the gas under consideration. Then, since the arrangement is such as to preclude convection currents the number of molecules moving along any given direction ( $cN_A |\bar{w}|$ )/6 is constant.<sup>9</sup> Any large surface in the gas, however, experiences a constant pressure ( $\propto cN_A |\bar{w}|^2$ ). Thus, through the body of the gas, there is an equilibrium of flow ( $c|\bar{w}| = \text{constant}$ ) and at the material surfaces there is equilibrium of pressure ( $c|\bar{w}|^2 = \text{constant}$ ). If a vane is placed in the gas perpendicular to the direction of the flow of heat the pressure will be constant over its surface except for a region at the edge of the vane in which there is a transition from equilibrium of pressure to equilibrium of flow. The width of this region is equal to the length of the mean free path of the gas.

The radiometer forces are therefore ascribed to the edge of the vane rather than its surface. Maxwell and Reynolds had previously suggested that this might be the case. Einstein concludes that forces of this type are represented

<sup>6</sup> *Phil. Trans. Roy. Soc.*, **170**, 231 (1880); *Scientific Papers* (London: Cambridge University Press, 1890), Vol. 2, p. 681.

<sup>7</sup> *Phil. Trans. Roy. Soc.*, **170**, 727 (1880); *Phil. Mag.*, **11**, 385 (1881); *Scientific Papers* (London: Cambridge University Press, 1900), Vol. 1, pp. 257 and 384.

<sup>8</sup> *Z. Physik*, **27**, 1 (1924).

<sup>9</sup> This consideration cannot be exact (Section 31) as it would lead to pressure differences in the gas.

by the equation

$$F = p\Lambda \frac{\Delta T}{T} \quad (40.1)$$

where  $F$  is the force per unit length of edge,  $p$  the pressure,  $\Lambda$  the mean free path and  $\Delta T$  the difference in temperature between the two sides of the vane. This equation can only account for positive radiometer forces. Since  $\Lambda$  is inversely proportional to the pressure it would seem that Equation (40.1) is in contradiction with the experimental results in that it predicts independence of  $F$  and  $p$ . Marsh,<sup>10</sup> however, has shown that  $\Delta T$  is inversely proportional to the pressure. He also demonstrated that the effect is determined by the edges rather than by the surface of the vane. This has also been done independently by I. Bleibaum.<sup>11</sup> She also showed that if Smoluchowski's equation for the abrupt temperature change at a surface (Section 32)

$$\Delta T = A\Lambda \frac{\partial T}{\partial x} \quad (40.2)$$

where  $A$  is a constant, be inserted in Equation (40.1) the resulting relation is

$$F = \frac{Ap\Lambda^2}{T} \frac{dT}{dx} \quad (40.3)$$

This equation has been thoroughly tested by Brüche and Littwin,<sup>12</sup> using an apparatus in which the temperature gradient could be carefully controlled. They verified the predictions of Equation (40.3) in that they found the force at high pressures to be proportional to the square of the mean free path, inversely proportional to the pressure and dependent upon the edge of the vane and not its surface.

Hettner<sup>13</sup> has derived Equation (40.3) from assumptions at first sight entirely different from those of Einstein. Hettner believes that radiometer forces are caused by temperature gradients tangential to the surface rather than normal to it. He points out that if such a gradient exists along a surface in contact with a gas, the gas is set in motion (thermal flow, Equation [35.10]). The radiometer forces are due to the reaction of this flow of gas. This had previously been suggested by Reynolds, as pointed out above, but the latter failed to carry the idea to its quantitative conclusion. Czerny and Hettner (*loc. cit.*) have shown the calculated forces to be present when a tangential temperature gradient is maintained in the radiometer vane. Hettner spoke of the phenomenon as a "thermal slip." He stated that the edges of the vane and any points or projections will be at a lower temperature than the rest of the vane due to their better thermal conductivity. A flow of gas is then set up from

<sup>10</sup> H. Marsh, E. Condon, and L. Loeb, *J. Opt. Soc. Am.*, **11**, 257 (1925); H. Marsh, *ibid.*, **12**, 135 (1926).

<sup>11</sup> *Z. Physik*, **49**, 590 (1928).

<sup>12</sup> *Z. Physik*, **52**, 318, 334 (1928). Cf. also P. Schmudde, *ibid.*, **53**, 331 (1929).

<sup>13</sup> *Ibid.*, **27**, 12 (1924); **37**, 179 (1926); **47**, 499 (1928); *Ergeb. exakt. Naturw.*, **7**, 209 (1928).

the cold to the hot regions and the vane is set in motion by the reaction of this flow.

Hettner applied his ideas to the various designs of radiometers. In all cases he considered the problem to be hydrodynamic in nature. He regarded his thermal slip and Einstein's edge effect to be different descriptions of the same phenomenon. Since they lead to the same equation, the experimental data cannot decide between the two.

Gerlach and Schütz<sup>14</sup> have succeeded in proving the existence of the flow of the gas along the surface experimentally. They used thin platinum foils, blackened on one side, and illuminated the blackened side. The temperature distribution was determined by small thermoelements, the flow by a little vane, the plane of which was normal to the plane of the radiometric plate, so that any gas flow parallel to the radiometric plate would deflect the vane. This flow was found, going from the cold backside around the edge to the hot middle of the frontside. The middle of the frontside is hotter, because the edge is better cooled, but the temperature difference for a given illumination varies in rather complicated manner with the pressure, due to the interaction of heat conduction in the gas and in the plate and the flow. As function of  $\log p$ , the flow has a maximum for a certain pressure and decreases symmetrically on both sides.

The exact mathematical theory for high pressure has been developed by Epstein<sup>15</sup> and Sexl.<sup>16</sup> Epstein used the formula (35.10) for the tangential velocity of the gas at the surface. His general procedure was first to solve the heat conduction problem; then, when the temperature distribution was known, the flow problem was solved like that of viscous flow, with (35.10) determining the border condition at the surface of the radiometer and no flow in infinity. When the hydrodynamic problem is solved, the force is calculated by integrating the stresses over the surface of the radiometer, the stresses being determined by the flow according to the hydrodynamical expressions. Of course, there exist also stresses directly due to the temperature gradient, but Epstein proved that they do not give a resultant force, in agreement with Maxwell's result.

For a sphere of heat conductivity  $\lambda_i$  and radius  $r_0$  in an external temperature gradient  $\partial T/\partial z$  the force turns out to be

$$F = \frac{9\pi\lambda r_0}{2\lambda + \lambda_i} \frac{\eta^2}{\rho_0 T_0} \frac{\partial T}{\partial z} \quad (40.4)$$

Since for this case ( $\alpha > \Lambda$ ) Stokes's law (29.10) gives a resistance which is also proportional to  $r_0$ , the velocity  $W$  which the particle attains in the temperature gradient is independent of  $r_0$ ; thus,

$$W = \frac{3}{2} \frac{\lambda}{2\lambda + \lambda_i} \frac{\eta}{\rho_0 T_0} \frac{\partial T}{\partial z} \quad (40.5)$$

<sup>14</sup> *Z. Physik*, **78**, 43 (1932).

<sup>15</sup> *Z. Physik*, **54**, 537 (1929).

<sup>16</sup> *Ibid.*, **52**, 249 (1928).

Rosenblatt and La Mer<sup>17</sup> have confirmed the theory experimentally and extended its range.

The discussion has so far been confined to regions of high or low pressures. In the former case the force varies as  $1/p$ ; in the latter it is proportional to  $p$ . Hettner,<sup>18</sup> and Brüche and Littwin (*loc. cit.*) have investigated the region of intermediate pressures where the mean free path of the gas is of the same order of magnitude as the dimensions of the body experiencing the radiometric force.

To find a formula covering the whole range, the force is represented by

$$\frac{1}{F} = \frac{a}{p} + \frac{p}{b} \quad (40.6)$$

where  $a$  and  $b$  are constants depending on the design of the radiometer, the temperature and the nature of the gas. For low pressures this formula is reduced to

$$1/F = a/p \quad \text{or} \quad F = p/a \quad (40.7)$$

which is identified with the Knudsen force. For high pressures, similarly,

$$1/F = p/b \quad \text{or} \quad F = b/p \quad (40.8)$$

which is identified with the Einstein-Hettner force. Equation (40.6) gives a maximum force at

$$p = (ab)^{\frac{1}{2}}$$

The existence of this maximum is in agreement with the measurements of Gerlach and of Westphal.<sup>19</sup> Hettner also showed that Equation (40.6) represents very well the pressure dependence of photophoresis, as measured by Mattauch.<sup>20</sup>

Rasmussen<sup>21</sup> has investigated a one-plate radiometer in the form of a strip going down the center of a cylindrical vessel of diameter  $d$ . The strip, of width  $B$ , is kept at a temperature different, by the amount  $\Delta T$ , from that of the wall. Following a method of Knudsen one side of the band is blackened; this is intended to make the accommodation coefficients of the two sides,  $f'$  and  $f''$ , different. This results in different pressures on the two sides and a resultant force  $F$  per unit length. It is readily shown that with this arrangement (if  $f = 1$  for the wall) the excess force on one side is, for the Knudsen case,  $f' - f''$  times (38.3) per unit area. However, there does not exist any detailed kinetic theory of the one plate radiometer, except for Weber's statement (see later) that his theory of the two plate radiometer can be applied here also.

We turn now to the behavior of the two plate radiometer (Knudsen's absolute radiometer) at intermediate pressures. Martin<sup>22</sup> investigated experi-

<sup>17</sup> *Phys. Rev.*, **70**, 385 (1946).

<sup>18</sup> M. Czerny and G. Hettner, *Z. Physik*, **30**, 258 (1926).

<sup>19</sup> W. Westphal, *ibid.*, **1**, 92, 431 (1920); **4**, 221 (1920); W. Gerlach, *ibid.*, **2**, 207 (1920).

<sup>20</sup> *Ann. Physik*, **85**, 967 (1928).

<sup>21</sup> *Ibid.*, **22**, 643 (1935).

<sup>22</sup> *Phil. Mag.*, **9**, 97 (1930). For dependence on the size of the plates, see E. Fredlund, *Ann. Physik*, **30**, 99 (1937).

mentally and theoretically the force between a hot and cold surface of only 2 mm<sup>2</sup> with distances  $d$  from 3 to 8 mm and pressure of a few hundredths of 1 mm of mercury.

An extensive investigation of the Knudsen manometer (two-plate radiometer) was undertaken by Weber,<sup>23</sup>

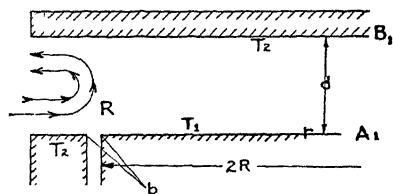


FIG. 29. Gas Flow in Knudsen's Absolute Manometer.

covering the whole pressure range. For intermediate pressures, the forces are due here also to a flow set up in the gas. Figure 29 shows a part of Fig. 28 with the cold plate  $B_1$ , the hot block  $A_1$  and the guard ring  $C_1$ . The distance from the center is  $r$ ,  $z$  is the coordinate normal to the plates,  $W$  the speed of the flow in the radial direction, and  $d$  the distance

between the plates. The equation of motion is then

$$\eta \frac{\partial^2 W}{\partial z^2} = \frac{\partial p}{\partial r} \quad (40.9)$$

as the pressure gradient drives the gas against the friction.

The total flow through any cross section must be zero. The condition along the lower boundary is

$$W - k_2 \frac{\eta}{\eta_e} \frac{\partial W}{\partial z} = \frac{3}{4} k_1 \frac{\eta}{\rho T} \frac{\partial T}{\partial r} \frac{1}{1 + \frac{\Lambda}{d}} \quad (40.10)$$

This is a modified Equation (35.8), the second term taking care of the slip; both terms are modified by constants  $k_1$ ,  $k_2$  introduced for experimental reasons, while the last factor is deduced theoretically (see Section 24). Upon integration, the flow velocity  $W$  appears as a quadratic function of  $z$ . This is introduced in Equation (40.9), to give  $\partial p / \partial r$ . Weber then assumed that the temperature difference (and therefore the pressure gradient) lay completely within the narrow airgap between the hot block  $A_1$  and the guard ring  $C_1$ , so that the gas flow did not penetrate into the space between the plates  $A_1$  and  $B_1$ . Then, using a method of Debye<sup>24</sup> and an empirical correction of the type mentioned in connection with (27.19), Weber found for the force per unit area an expression which can be written

$$F = \frac{\Delta T}{4T} p \left[ 1 + \frac{3d}{4\Lambda} + 0.0065 \left( \frac{d}{\Lambda} \right)^2 \frac{1.3 - 4.6d/\Lambda}{1 - 0.46d/\Lambda} \right] \quad (40.11)$$

This agrees very well with Knudsen's<sup>25</sup> measurements.

<sup>23</sup> *Kgl. Danske Videnskab. Selskab. Math.-fys. Medd.*, 14, 13 (1937).

<sup>24</sup> *Physik. Z.*, 11, 1115, 1260 (1910).

<sup>25</sup> *Ann. Physik*, 32, 831 (1910).

(41) **Influence of Magnetic and Electric Fields on Heat Conduction and Viscosity:** Senftleben<sup>1</sup> discovered that a magnetic field diminishes heat conduction for some paramagnetic gases (O<sub>2</sub>, NO, but not Na). In most experiments, the magnetic field is at right angles to the temperature gradient; for other directions the value of the effect is different. For the usual arrangement,  $-\Delta\lambda/\lambda$ , where  $\Delta\lambda$  is the change in heat conduction, depends only on  $H/p$ , where  $H$  is the magnetic field, and  $p$  is the gas pressure. This is true provided the mean free path is small compared with the dimensions of the vessel.<sup>2</sup>

For constant  $p$ ,  $-\Delta\lambda/\lambda$  increases first quadratically with  $H$ , then comes a linear part, until at high values of  $H/p$  ( $\sim 11,000$  Gauss at 100 mm of mercury for O<sub>2</sub>)  $-\Delta\lambda/\lambda$  approaches a saturation value of about 1.1 per cent.

A similar effect on viscosity was found by Engelhardt and Sack.<sup>3</sup> The qualitative behavior appeared to be similar to the case of heat conduction. After it had been realized that in viscous flow corrections must be made to the pressure measurements on account of the viscous stresses, it was found that for the same value of  $H/p$ ,  $-\Delta\eta/\eta$  is nearly proportional to  $-\Delta\lambda/\lambda$ . The following results, for example, have been obtained:<sup>4</sup>

Gas	O <sub>2</sub>	O <sub>2</sub>	NO	NO
$H/p$	2.5	20	15	40
$\frac{\Delta\lambda}{\lambda} : \frac{\Delta\eta}{\eta}$	2.0	1.85	1.77	1.7

As an explanation of the phenomenon, Senftleben and his students have assumed a shortening of the mean free path by the field. Gorter has ascribed this to the precession of the molecules set up by the field.<sup>5</sup> Laue<sup>6</sup> elaborated this assumption into a formal consideration of the possible dependence of the effects on the angle between field and gradient.

An electric field in the direction of a temperature gradient increases heat conduction.<sup>7</sup> This occurs only in the presence of convection currents.<sup>8</sup> The effect has been explained as due to local differences in electrostriction.<sup>9</sup> Dipolar gases show the effect more strongly.<sup>9a</sup>

<sup>1</sup> *Physik. Z.*, **31**, 822, 961 (1930); **32**, 550 (1931); **33**, 177 (1932); **34**, 230 (1933); H. Senftleben and J. Pietzner, *ibid.*, **35**, 386 (1934).

<sup>2</sup> H. Senftleben and J. Pietzner, *Ann. Physik*, **27**, 108 (1936).

<sup>3</sup> *Physik. Z.*, **33**, 724 (1932); M. Trautz and E. Fröschel, *Ann. Physik*, **22**, 223 (1935).

<sup>4</sup> H. Senftleben and H. Gladisch, *Ann. Physik*, **30**, 713 (1937).

<sup>5</sup> C. J. Gorter, *Naturwiss.*, **26**, 140 (1938); F. Zernike and C. van Lier, *Physica*, **6**, 961 (1939).

<sup>6</sup> *Ann. Physik*, **23**, 1 (1935); **26**, 474 (1936).

<sup>7</sup> W. Bonwitt and G. Groetzinger, *Z. Physik*, **72**, 600 (1931); H. Senftleben, *Physik. Z.*, **32**, 500 (1931); *Z. Physik*, **74**, 757 (1932).

<sup>8</sup> H. Senftleben, *Physik. Z.*, **33**, 826 (1932); **35**, 661 (1934); H. Senftleben and W. Braun, *Z. Physik*, **102**, 480 (1936).

<sup>9</sup> A quantitative theory has been given by H. Senftleben and H. Gladisch, *Z. Physik*, **126**, 239 (1949).

<sup>9a</sup> G. Groetzinger and R. Frey, *Physik. Z.*, **36**, 292 (1935); H. Senftleben, *ibid.*, **36**, 297 (1935); E. W. Becker, *Z. Naturforsch.*, **2a**, 297 (1947).



Senftleben<sup>10</sup> has also found a slight diminution of the diffusion of  $\text{CCl}_4$  (diamagnetic) in  $\text{O}_2$  through a magnetic field.

#### DIFFUSION

(12) **Kinetic Theory of Diffusion:** When the kinetic theory was first proposed it met with the objection that, if the molecules actually have velocities of several hundred meters per second, gases should spread almost instantaneously, whereas it was well known that if hydrogen sulfide is set free in one corner of a room, several minutes elapse before it can be smelled in the opposite corner. This criticism was soon answered by Clausius who pointed out that the molecules of the foreign gas cannot move in a straight line from one corner of the room to the other but that, on the contrary, as a result of collisions with the air molecules already in the room, they move in a zig-zag path. Their actual path from one point to another is incomparably greater than the rectilinear distance between the two points, provided this distance is large in comparison to the mean free path. According to the theory of Brownian motion, the linear distance between two points is approximately the geometrical mean between  $\Lambda/3$  and the actual distance traveled by the molecule. If the space were evacuated until the mean free path was large in comparison to the distance between the two points, the gas would actually distribute itself with its thermal velocity.

This slow interpenetration of the molecules of two different gases is called diffusion. For a long time the theory of the phenomenon has been presented in contradictory ways. The simplest case which can be calculated accurately is one in which certain molecules of a gas are supposed to be recognizable from the others (Einstein speaks of them in his lectures as being "colored red"). These marked molecules are identical with the unmarked in respect to mass and diameter. The problem is now to follow their motion (Maxwell's diffusion of a gas "into itself"). The diffusion of two isotopes into each other would illustrate the present situation approximately. The number of marked molecules passing upward through unit cross-section per sec is

$$\frac{|w|}{6} \cdot N_{Ac'-} \quad (42.1)$$

where  $N_{Ac'-}$  is the number of marked molecules per cc at a distance  $\Lambda$  from the area under consideration, or

$$N_{Ac'-} = \left( c' - \Lambda \frac{\partial c'}{\partial z} \right) N_A \quad (42.2)$$

Similarly the flow downward is

$$N_A \frac{|\bar{w}|}{6} \left( c' + \Lambda \frac{\partial c'}{\partial z} \right) \quad (42.3)$$

<sup>10</sup> *Physik. Z.*, **34**, 835 (1934).

and the net flow through unit area in unit time downward is

$$N_A \frac{w}{3} \Lambda \frac{\partial c'}{\partial z} \quad (42.4)$$

The same number of unmarked molecules passes through the same area in the opposite direction, the number being

$$\frac{|\bar{w}|}{3} \Lambda \frac{\partial c}{\partial z} N_A \quad (42.5)$$

Since, as a result of the equality of pressure throughout, the total density is everywhere the same,

$$c + c' = \text{constant} \quad (42.6)$$

so that

$$-\frac{\partial c}{\partial z} = \frac{\partial c'}{\partial z} \quad (42.7)$$

These two numbers are equal and the diffusion does not change the total pressure.

The diffusion constant  $D$  is defined from the relation giving the number of molecules diffusing through unit cross-section in unit time, which is

$$D \frac{\partial c}{\partial z} N_A \quad (42.8)$$

Therefore

$$D = \frac{w}{3} \Lambda = \frac{|w|}{3N_A(c + c')\pi d^2\sqrt{2}} \quad (42.9)$$

or

$$D = M(c + c') \quad (42.10)$$

Hence  $D$  is seen to be inversely proportional to the total concentration.

A more exact calculation both for  $\eta$  (Equation [21.7]) and  $D$  (Equation [42.10]) shows that this has to be replaced by

$$D = K \eta / \rho \quad (42.11)$$

where  $K$  depends on the law of interaction between the molecules and has been calculated for a potential energy of repulsion of the form  $A/r^s$ . The following shows the values to be used:

$s$	4		9	10	14	$\infty$	(hard elastic spheres)
$K$	1.504 *	1.49	1.44	1.41	1.37	1.200 *	

\* More exact than the other values.

Harteck and Schmidt<sup>1</sup> have measured the diffusion of para-hydrogen into normal hydrogen and found  $K = 1.37$ , corresponding to  $s = 14$ . Ney and Armistead<sup>2</sup> found for  $\text{UF}_6$  that  $K = 1.31$  and  $s = 19$ .

Boardman and Wild<sup>3</sup> have measured the diffusion constants of pairs of gases with molecules of equal mass, size and force field, namely  $\text{N}_2\text{--CO}$  and  $\text{N}_2\text{O--CO}_2$ . Applying Equation (42.11), they found for  $\text{N}_2\text{--CO}$ :  $K = 1.44$  and  $s = 9$ , and for  $\text{N}_2\text{O--CO}_2$ :  $K = 1.39$  and  $s = 14$ .

If the marked molecules are different from the others, the values for  $|w|$  and  $\Lambda$  for each molecular species must be distinguished by marking one set with primes. There is then obtained for the number of molecules of the first kind diffusing downward

$$\frac{|\bar{w}'|}{3} \Lambda' \frac{\partial c'}{\partial z} N_A \quad (42.12)$$

and for the number of molecules of the second kind diffusing upward

$$- \frac{|\bar{w}|}{3} \Lambda \frac{\partial c}{\partial z} N_A \quad (42.13)$$

The mean free path is given by Equation (11.15),

$$\Lambda' = \frac{1}{\pi N_A \left[ d'^2 \sqrt{2} c' + \left( \frac{d + d'}{2} \right)^2 c \sqrt{\frac{m + m'}{m}} \right]} \quad (42.14)$$

$$\Lambda = \frac{1}{\pi N_A \left[ d^2 \sqrt{2} c + \left( \frac{d + d'}{2} \right)^2 c' \sqrt{\frac{m + m'}{m'}} \right]} \quad (42.15)$$

The two currents of gas are in general of different amount so that an excess flow downward of magnitude

$$N_A \left( \frac{|\bar{w}'| \Lambda'}{3} - \frac{|\bar{w}| \Lambda}{3} \right) \frac{\partial c'}{\partial z} \quad (42.16)$$

is set up. As before, this is obtained from the fact that

$$\frac{\partial c'}{\partial z} = - \frac{\partial c}{\partial z} \quad (c' + c = \text{const.}) \quad (42.17)$$

This effect would soon disturb the initial condition of equality of total pressure if the process took place in a closed tube. O. E. Meyer<sup>4</sup> assumed, therefore,

<sup>1</sup> *Z. physik. Chem.*, **B**, 21, 447 (1933). Attention should be called to the fact that our  $s$  refers to the energy, theirs to the force; our  $s$  is therefore smaller by unity.

<sup>2</sup> *Phys. Rev.*, **71**, 14 (1947).

<sup>3</sup> *Proc. Roy. Soc.*, **A**, 162, 511 (1937).

<sup>4</sup> O. E. Meyer, *Kinetische Theorie der Gase* (1st ed.; Breslau: 1877). For a criticism of this and other approximate theories see S. Chapman, *Phil. Mag.*, **5**, 630 (1928).

that, in order to preserve the constancy of pressure, there is superimposed upon the calculated process a flow of the gas as a whole upward which just compensates the flow given by (42.16). Since the gas at the point under consideration is made up of a fraction  $c'/(c+c')$  of molecules of the first kind and a fraction  $c/(c+c')$  of molecules of the second kind, the equalizing flow upward of molecules of the first species equals

$$N_A \left( \frac{|\bar{w}'|\Lambda'}{3} - \frac{|\bar{w}|\Lambda}{3} \right) \frac{c'}{c+c'} \cdot \frac{\partial c'}{\partial z} \quad (42.18)$$

Similarly the corresponding flow of molecules of the second species upward is

$$N_A \left( \frac{|\bar{w}'|\Lambda'}{3} - \frac{|\bar{w}|\Lambda}{3} \right) \frac{c}{c+c'} \frac{\partial c'}{\partial z} \quad (42.19)$$

The total flow through unit cross section in unit time downward is therefore

$$\left. \begin{aligned} N_A \frac{|\bar{w}'|\Lambda'}{3} \cdot \frac{\partial c'}{\partial z} - N_A \left( \frac{|\bar{w}'|\Lambda'}{3} - \frac{|\bar{w}|\Lambda}{3} \right) \frac{c'}{c+c'} \cdot \frac{\partial c'}{\partial z} \\ N_A \left[ \frac{|\bar{w}'|\Lambda'}{3} \cdot \frac{c}{c+c'} + \frac{|\bar{w}|\Lambda}{3} \cdot \frac{c'}{c+c'} \right] \frac{\partial c'}{\partial z} \end{aligned} \right\} \quad (42.20)$$

molecules of the first kind and upward

$$\left. \begin{aligned} N_A \frac{|\bar{w}'|\Lambda'}{3} \cdot \frac{\partial c'}{\partial z} + N_A \left( \frac{|\bar{w}'|\Lambda'}{3} - \frac{|\bar{w}|\Lambda}{3} \right) \frac{c}{c+c'} \cdot \frac{\partial c'}{\partial z} \\ N_A \left[ \frac{|\bar{w}'|\Lambda'}{3} \cdot \frac{c}{c+c'} + \frac{|\bar{w}|\Lambda}{3} \cdot \frac{c'}{c+c'} \right] \frac{\partial c'}{\partial z} \end{aligned} \right\} \quad (42.21)$$

molecules of the second kind. The diffusion coefficients of the two kinds have become equal, as must be the case if there is to be no unidirectional flow,

$$D' = D = \frac{|\bar{w}'|\Lambda'}{3} \frac{c}{c+c'} + \frac{|\bar{w}|\Lambda}{3} \frac{c'}{c+c'} \quad (42.22)$$

However, they depend on the ratio of the concentrations  $c'/c$  and change from place to place of the diffusing column.<sup>5</sup>

Gross<sup>6</sup> believed that the back flow could be neglected in the case of open tubes, retaining Equations (42.4) and (42.5). There is then also obtained a dependence upon the ratio of concentrations but it is not as pronounced as in Meyer's development and is of the opposite sign (i.e., according to one formula  $D$  should increase with increasing  $c'$ , according to the other it should decrease but to a less extent). The experimental side of the problem was not settled for a long time. It was only known that the dependence was not as great as

<sup>5</sup> Cf. J. H. Jeans, *The Dynamical Theory of Gases* (4th ed.; London: Cambridge Univ. Press, 1925), Chapter XIII.

<sup>6</sup> *Wied. Ann.*, 40, 424 (1890).

that required by (42.22) but whether or not it was present in general was not decided. A series of very careful experiments have shown (in the case of mixtures of  $\text{H}_2\text{--O}_2$ ,  $\text{N}_2\text{--H}_2$ ,  $\text{O}_2\text{--N}_2$ ,  $\text{H}_2\text{--CO}_2$ ,  $\text{A--He}$ ) that there is a slight dependence, the direction of which is correctly given by O. E. Meyer's equation, but which is much smaller than that calculated. For example, in a 50 per cent  $\text{A--He}$  mixture  $D$  was found to be 0.25405, calculated 0.2537; for  $\text{A/He} = 0.377$ , found 0.25040, calculated, 0.208. Gross's formula gives the order of magnitude about correctly.<sup>7</sup>

In contrast to these equations Stefan<sup>8</sup> has deduced formulas according to which  $D$  does not depend on the ratio of the concentrations. His results, however, are not obtained from a purely molecular theory. Consider<sup>9</sup> a gas mixture in which the unprimed gas has a concentration gradient  $\partial c/\partial z$  and therefore a gradient  $\partial p/\partial z$  of the partial pressure  $p(p = cRT)$ . The force acting on the unprimed component contained in one cubic centimeter is  $-\partial p/\partial z$ , which produces a flow of this component of velocity  $W$ . The other component moves in the opposite direction with velocity  $W'$ , driven by the force resulting from the primed pressure gradient  $\partial p'/\partial z$ . The stationary state is attained because of the frictional force due to the movement of the two gas components against each other. This frictional force, which will be discussed below from the physical standpoint, is written  $A_{12}cc'(W' - W)$  and hence

$$-\partial p/\partial z = A_{12}cc'(W' - W) = \partial p'/\partial z \quad (42.23)$$

From this it follows

$$p + p' = \text{constant}; \quad c + c' = \text{constant} = c_0, \quad (42.24)$$

$c_0$  being the molar concentration of the whole gas.

The equation of continuity which states that, at the stationary state, just as much gas enters any element of volume as leaves it, here takes the form

$$c'W' = \text{constant}; \quad cW = \text{constant}, \quad (42.25)$$

and since there is no flow of the gas as a whole,

$$c'W' + cW = 0 \quad (42.26)$$

There follows further

$$\left. \begin{aligned} -RT \frac{\partial c'}{\partial z} &= RT \frac{\partial c}{\partial z} = A_{12}[c'W'c - cWc'] \\ &= A_{12}[(c'W')(c_0 - c') - (cW)c'] \end{aligned} \right\} \quad (42.27)$$

or

$$-\frac{\partial c'}{\partial z} = \frac{\partial c}{\partial z} = \frac{A_{12}}{RT}[c'W'c_0 - (c'W' + cW)c'] = \frac{A_{12}}{RT}c'W'c_0 \quad (42.28)$$

<sup>7</sup> Summarized by A. Lonius, *Ann. Physik*, 29, 664 (1909).

<sup>8</sup> *Wien. Ber.*, 65, 323 (1872); J. C. Maxwell, *Phil. Mag.*, 35, 129 (1868).

<sup>9</sup> This follows a presentation by W. H. Furry, *Amer. J. Physics*, 16, 63 (1948).

The amount passing through unit area in unit time is then

$$c'W' = \frac{-RT}{A_{12}c_0} \frac{\partial c'}{\partial z} \quad (42.29)$$

which is equal to

$$-cW = \frac{RT}{A_{12}c_0} \frac{\partial c}{\partial z} \quad (42.30)$$

The common coefficient of diffusion is  $D = RT/c_0A_{12}$  and is seen to be independent of the ratio of the concentrations. The quantity  $A_{12}$  is found by calculating the momentum transferred between the molecules of the two kinds by the relative <sup>10</sup> flow  $W' - W$ . If we assume first hard, incompressible molecules, and, for the moment, consider the primed component at rest, an unprimed molecule, hitting it, will first be stopped and transfer a linear momentum of (on the average)  $mW$  and then fly off under an angle of deflection  $\psi$  and transfer, in the original direction, the moment  $-mW \cos \psi$  (the components normal to the flow direction will cancel out). If  $dQ$  is an element of the collision cross-section which gives a deflection  $\psi$ , we define a "diffusion cross-section" <sup>11</sup>

$$Q_D = \int dQ(1 - \cos \psi) \quad (42.31)$$

The momentum transferred per second and cubic centimeter is therefore <sup>12</sup>

$$N_A c_2 \left( \frac{kT}{2\pi m} \right)^{\frac{1}{2}} m W N_A c' Q_D \quad (42.32)$$

Since both gases move,  $m$  must be replaced by the effective mass  $\bar{m}$  (Section 4) and  $W$  by  $W - W'$ ; hence

$$A_{12} = 2N_A^2 \left( \frac{kT\bar{m}}{2\pi} \right)^{\frac{1}{2}} Q_D = 2 \left( \frac{RT\bar{M}}{2\pi} \right)^{\frac{1}{2}} N_A Q_D \quad (42.33)$$

The result becomes somewhat more complicated, if the molecules are not rigid, since then  $Q_D$  depends on the velocities and has to be properly integrated. If there exists a potential energy of repulsion of the form  $B/r^s$  (see Section 21) between the molecules, the cross-section  $Q_D$ , which has dimensions  $r^2$ , is proportional to

$$\left( \frac{B}{m} \right)^{2/s} w^{-4/s} \quad (42.34)$$

<sup>10</sup> Furry points out that the use of the mean free path in (42.12) is misleading since only the motion of the two gas components in respect to each other matters.

<sup>11</sup> To be distinguished from a "viscosity cross-section."

<sup>12</sup> The factor 2 is due to the fact that the flow affects both the collision rate and the momentum transferred.

The number of molecules of relative velocity  $w$  colliding per sec. is, therefore, proportional to

$$wQ_D \propto \left(\frac{B}{m}\right)^{2/s} w^{1-4/s} \quad (42.35)$$

If  $s = 4$  (Maxwellian molecules), the number of colliding molecules is independent of the molecular velocity  $W$  and the velocity distribution function need not be known. There is then obtained the exact relationship,

$$D = \frac{kT}{m(c + c')} (N_A w Q_D)^{-1} \quad (42.36)$$

as Maxwell first showed.<sup>13</sup>

For  $s$  different from 4, distribution functions of the type (29.8) are used for both gases; thus,

$$f = N_A c \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{mw^2}{2kT}} \left(1 - \frac{m}{kT} \zeta W\right) d\xi d\eta d\zeta \quad (42.37)$$

and for  $A_{12}$  ( $\tilde{w}$  = relative velocity, see [4.4])

$$(W' - W)A_{12} = N_A^2 \bar{m} \int f d\xi d\eta d\zeta \int f' d\xi' d\eta' d\zeta' \tilde{w} Q_D(\zeta' - \zeta) \quad (42.38)$$

By transforming to the components of the velocity of the center of gravity and the relative velocity as in (4.3), (4.4) we find

$$D = \frac{3kT}{[16\bar{m}N_A(c + c')]} [\Omega_{12}^{(1)}(1)]^{-1} \quad (42.39)$$

where

$$\Omega_{12}^{(1)}(1) = \frac{1}{2}\pi^{-\frac{1}{2}} \int e^{-\frac{mw^2}{2kT}} \left(\frac{\bar{m}w^2}{2kT}\right)^4 \left(\frac{\bar{m}}{2kT}\right) dw \int w(1 - \cos\psi) dQ \quad (42.40)$$

$D$  is, according to (42.39), independent of the composition. For hard elastic molecules,

$$[\Omega_{12}^{(1)}(1)]^{-1} = \left(\frac{\bar{m}}{2\pi kT}\right)^{\frac{3}{2}} \frac{8}{(d + d')^2} \quad (42.41)$$

Hirschfelder and his coworkers<sup>13a</sup> have evaluated the diffusion coefficient (42.39) from their tables for the computation of  $\Omega$  (see Section 17), using the Lennard-Jones interaction potential

$$4\epsilon_{12} \left[ \left(\frac{r_{12}}{r}\right)^{12} - \left(\frac{r_{12}}{r}\right)^6 \right]$$

They use

$$r_{12} = \frac{1}{2}(r_0^{(1)} + r_0^{(2)}) \quad (\text{see Section 23})$$

<sup>13</sup> *Scientific Papers*, Vol. 2, p. 26.

<sup>13a</sup> J. O. Hirschfelder, R. B. Bird and E. L. Spotz, *Chem. Rev.*, **44**, 205 (1949); *Trans. Am. Soc. Mech. Eng.*, **71**, 921 (1949).

and then calculate  $\epsilon_{12}$  from  $D$ . For self-diffusion where  $\epsilon_{12}$  (here  $\epsilon$ ) is known from viscosity (Section 21) and  $r_{12} = r_0$ , the agreement between theory and experiment is fairly good. For two different gases, there is shown below a comparison of  $\epsilon_{12}$  as determined from  $D$  and as determined by the approximation  $\epsilon_{12} = \sqrt{\epsilon_1 \epsilon_2}$  (Section 23) for some gases.

Gases	He-A	H <sub>2</sub> -O <sub>2</sub>	H <sub>2</sub> -N <sub>2</sub>	O <sub>2</sub> -CO	O <sub>2</sub> -CO <sub>2</sub>
$\epsilon_{12}/k$ from $D$	24.5	58.2	46.1-47.8	91.9	110-115
$\sqrt{\epsilon_1 \epsilon_2}/k$	27.3	61.4	55.2	112	147

By going to the next higher approximation these authors have also discussed the dependence of  $D$  on the composition (see below).

Boltzmann<sup>14</sup> confirmed after a lengthy calculation, that the diffusion coefficient for elastic spheres is independent of the ratio of concentrations. More recently Langevin<sup>15</sup> has also stated this independence. Finally the rigorous method of Enskog leads, in lowest approximation, to (42.39) and (42.40).

Equation (42.39), which requires that  $D$  be independent of the ratio of concentrations, is only a first approximation. The second approximation introduces on the right hand side the factor

$$1 + \frac{A_{II} \left(1 + \beta_{II} \frac{c}{c'}\right) + A'_{II} \left(1 + \beta'_{II} \frac{c'}{c}\right) - 52A_{II}A'_{II}}{\left(1 + \beta_{II} \frac{c}{c'}\right)\left(1 + \beta'_{II} \frac{c'}{c}\right) - 676A_{II}A'_{II}} \quad (42.42)$$

$$\text{where} \quad \beta_{II} = \left(\frac{2d}{d+d'}\right)^2 \sqrt{\frac{m+m'}{2m'}} \frac{4(m+m')^2}{15m^2 + 8mm' + 6m'^2} \quad (42.43)$$

$$\beta'_{II} = \left(\frac{2d'}{d+d'}\right)^2 \sqrt{\frac{m+m'}{2m'}} \cdot \frac{4(m+m')^2}{6m^2 + 8mm' + 15m'^2} \quad (42.44)$$

$$A_{II} = \frac{m'^2}{12m^2 + 16mm' + 30m'^2} \quad (42.45)$$

$$A'_{II} = \frac{m^2}{30m^2 + 16mm' + 12m'^2} \quad (42.46)$$

The experimental results are well represented by this equation.

Enskog gives the following table for the diffusion constant of a mixture of gases 1 and 2 in the ratio three to one ( $D_{(3/1)}$ ) compared with the diffusion constant in a mixture in which the ratio is one to three, ( $D_{(1/3)}$ ).

<sup>14</sup> *Wien. Ber.*, 86, 63 (1882); 88, 835 (1883); *Ges. Abh.*, 3, 3, 63.

<sup>15</sup> *Ann. chim. phys.*, 5, 245 (1905).



Gas 1.....	A He	O <sub>2</sub> H <sub>2</sub>	CO <sub>2</sub> H <sub>2</sub>
Gas 2.....			
$\frac{D_{(3/1)}}{D_{(1/3)}} (\text{exp.})^1$ .....	1.11	1.048	1.067
$\frac{D_{(3/1)}}{D_{(1/3)}} (\text{theor.})$ .....	1.072	1.076	1.078

<sup>1</sup> A. Lonius, *loc. cit.*; S. Rosseland, *Physica*, 5, 381 (1925).

Hellund<sup>17</sup> has treated diffusion in ternary mixtures. New phenomena occur then; e.g., if gas A contains in one part an admixture of B, in another part an admixture of C, the mutual diffusion of B and C will exert a force on gas A, which was originally uniformly distributed, and set it in motion.

Gilliland<sup>18</sup> has given a method for calculating the diffusion constant from the chemical formula of the gas. For this purpose, he follows a suggestion of Titani,<sup>19</sup> that the molecular radius  $d$  is proportional to the cube root of  $V$ , where  $V$  is the molar volume of the liquid at its normal boiling point. Then the expression  $(d + d')^2$  in the denominator of (42.31) is replaced by  $(V_1^{\frac{1}{3}} + V_2^{\frac{1}{3}})^2 \times \text{constant}$ , and  $D$  can be written

$$D = \frac{0.0043T^{\frac{3}{2}}}{(V_1^{\frac{1}{3}} + V_2^{\frac{1}{3}})^2 p} \sqrt{\frac{M_1 M_2}{M_1 + M_2}} \quad (42.47)$$

As the  $V$ 's are not always known, they are calculated for organic compounds additively according to their constitution.<sup>20</sup>

The constant 0.0043 is empirically determined and is only about 2/3 of the one that would be expected from (42.31) and Titani's constant. About 500 pairs of substances were tested, ranging from air-H<sub>2</sub>, air-Hg, and He-A to organic compounds, as in the pair air-amyl butyrate. The agreement is quite good, somewhat better than if a factor  $(1 + C/T)^{-1}$  is introduced in (42.47) (see Equation [13.10]).

(43) **The Diffusion Slip:** Kramers and Kistemaker<sup>1</sup> have discovered a phenomenon analogous to slip (Section 24) and temperature jump if there exists in a mixture a concentration gradient tangential to a solid wall. In this case a flow is set up analogous to the flow in case of a temperature gradient (Sections 35, 36). From Equations (42.23), (42.26) and (43.30), the resulting relative flow velocity of the two components in respect to each other is

$$\tilde{W} = W' - W = - \frac{(c + c')}{cc'} D \frac{\partial c}{\partial z} \quad (43.1)$$

<sup>17</sup> *Phys. Rev.*, 57, 319, 737 (1940).

<sup>18</sup> *Ind. Eng. Chem.*, 26, 681 (1934).

<sup>19</sup> *Bull. Soc. Chem. Japan*, 8, 255 (1930).

<sup>20</sup> J. H. Arnold, *Ind. Eng. Chem.*, 22, 1091 (1930); *J. Chem. Phys.*, 1, 220 (1933).

<sup>1</sup> *Physica*, 10, 699 (1943).

and the mass flow is

$$W_M = \frac{(c'M'W' + cMW)}{(cM + c'M')} - \frac{(M' - M)}{(cM + c'M')} D \frac{\partial c}{\partial x} \quad (43.2)$$

This is the velocity which enters into the hydrodynamic Equations (17.3), (17.4) and (17.5).

According to the arguments of Section 24 the slip velocity at the wall is equal to the full flow velocity of the gas in the case in which no tangential momentum is transferred from the gas to the wall. This argument is used here; the conditions are found under which no tangential momentum is transferred to the wall from the diffusing gas, and conclusions are then drawn about slip velocity.

Assume a wall, with accommodation coefficient  $f = 1$ , which moves in its own plane with a velocity  $W_0$  in the  $z$ -direction,  $W_0$  being such that no tangential momentum is transferred to it from the diffusing gas. To calculate the effect, we first assume Maxwellian molecules (energy of repulsion proportional to  $r^{-4}$ ). In this case the effect of diffusion on the distribution of molecular velocities is exactly given by the superposition of flow velocities  $W$  and  $W'$  (see Section 42).

If the tangential momentum transferred to the wall is to be zero, the molecules hitting the wall have to bring in exactly the same amount of the  $z$ -component of linear momentum as the molecules leaving the wall carry away. Therefore,

$$\frac{1}{4} |w'| c' M' W' - \frac{1}{4} |w| c M W = \left( \frac{1}{4} |w'| c' M' + \frac{1}{4} |w| c M \right) W_0 \quad (43.3)$$

or

$$W_0 = \frac{(\sqrt{M'} - \sqrt{M})}{(c\sqrt{M} + c'\sqrt{M'})} D \frac{\partial c}{\partial z} \quad (43.4)$$

If the wall moved with speed  $W_0$ , the slip would be equal to  $W_M$  (Equation [43.2]). Since the wall is at rest, the slip is only

$$W_s = W_M - W_0 = \left[ \frac{(M' - M)}{(cM + c'M')} - \frac{(\sqrt{M'} - \sqrt{M})}{(c\sqrt{M} + c'\sqrt{M'})} \right] D \frac{\partial c}{\partial z} \quad (43.5)$$

and a tangential force equal to the left side of (43.3) is exerted on the wall. For non-Maxwellian molecules, the results differ only by a few percent. If diffusion takes place in a closed, e.g., cylindrical, tube, the situation is similar to that described in Section 35. Since the diffusing gas exerts a tangential force on the wall, the wall exerts an equal and opposite stress on the gas, which results in a flow of the gas along the wall; in the closed tube, there must be an opposing flow in the center, resulting in a pressure difference. In a tube of diameter  $d$ ,

$$\frac{dp}{dz} = \frac{32\eta}{d^2} (W_M - W_0) \quad (43.6)$$

which upon integration gives, approximately, for the pressure difference

$$\Delta p = - \frac{32\eta D}{d^2} \ln (c\sqrt{M} + c'\sqrt{M'}) \Big] \quad (43.7)$$

where  $\Big]$  signifies that the difference of the values of the logarithms at the ends of the tube should be taken. Experiments by Kramers and Kistemaker for the diffusion of air against hydrogen gave values too small by about one third.

(44) **Theory of the Diffusion Pump:**<sup>1</sup> Consider a gas contained in a horizontal tube. The symbols referring to this gas will be designated by primes in the following discussion. Through this first gas a second diffuses from right to left. The properties of the second gas will be designated by two primes. The number of molecules of the second gas diffusing through unit area in unit time is

$$-D \frac{dc''}{dx} \quad (44.1)$$

Assume that the first gas is moving to the right with a velocity  $W$ .<sup>2</sup> Then the quantity of the second gas flowing to the right is  $c''W$  if no diffusion takes place and if both gases move together. Taking both effects into account the total flow of the second gas to the right is

$$c''W + D \frac{dc}{dx} \quad (44.2)$$

and of the first

$$c'W + D \frac{dc'}{dx} \quad (44.3)$$

Since

$$c' + c'' = \text{constant} = c_0 \quad (44.4)$$

the second expression becomes

$$c_0W - \left( c''W + D \frac{dc''}{dx} \right) \quad (44.5)$$

That is, the amount of the first gas flowing to the right equals the difference between the total amount flowing into the right and the amount of the second flowing to the right.

If a stationary state is assumed, equal amounts of each gas must flow through every cross section, whence

$$c''W + D \frac{dc''}{dx} = \text{constant} = B \quad (44.6)$$

<sup>1</sup> W. Gaede, *Ann. Physik*, **46**, 357 (1915); *Z. techn. Physik*, **4**, 337 (1923). For the pumps designed by Langmuir and others see S. Dushman, *Production and Measurement of High Vacuum* (Schenectady, 1922); J. Yarwood, *High Vacuum Technique* (2nd ed.; New York: John Wiley and Sons, 1943).

<sup>2</sup> In this section the magnitude of the velocity  $|W|$  will be written  $W$ .

or

$$c'' = \frac{B}{W} + \left( c_{x=0}'' - \frac{B}{W} \right) e^{-\frac{W}{D}x} \quad (44.7)$$

and if the concentration  $c_1''$  prevails at the point  $x_1$ ,

$$\frac{c''_1 - c''_0 e^{-\frac{W}{D}x_1}}{1 - e^{-\frac{W}{D}x_1}} \cdot W = B \quad (44.8)$$

In the integration of Equation (44.6) it is assumed that  $W$  and  $D$  are independent of  $x$ , which may or may not be justifiable according to the conditions of the flow.

If the diffusion of the second gas to the left is just compensated by its flow to the right  $B = 0$  and

$$W = \frac{D}{x_1} \ln \frac{c''_0}{c''_1} \quad (44.9)$$

The diffusion pump depends upon the principle discussed here, namely, that the diffusion of a gas caused by its own partial pressure gradient also takes place against the flow of another gas, if the latter is not too rapid. Consider two spaces  $A$  and  $B$  connected by means of a narrow tube.  $B$  is connected to the receiver to be evacuated and is therefore full of the gas which is to be pumped away (designated with the double prime). In  $A$  there is boiling mercury. The partial pressure of the gas to be pumped out is maintained lower in  $A$  than in  $B$  by the rapid stream of mercury vapor flowing past the mouth of the connecting tube. This stream entrains and carries away all the gas which diffuses through the tube. Of course the mercury vapor streams through the tube into  $B$  but, on account of the small diameter of the tube, this is not sufficiently rapid to prevent the diffusion in the reverse direction of the gas which is being removed. The partial pressure of the mercury vapor is maintained at a low value in  $B$  by continuous water cooling.

The pressures in common practice fall in the region intermediate between diffusion proper and Knudsen's effusion (Sections 25, 27). Gaede (*loc. cit.*) has carried out some calculations for the latter extreme case.<sup>3</sup>

Equation (44.9) may also be written

$$c_1'' = c_0'' e^{-\frac{Wx_1}{D}} \quad (44.10)$$

giving the concentration of the second gas diffusing against a flow of the first as a function of the distance and velocity of flow. This principle has been applied to the separation of gaseous mixtures, since the different constituents of the

<sup>3</sup> For a more detailed theoretical discussion, together with some experimental work see W. Molthan, *Z. techn. Physik*, 7, 377, 452 (1926). Cf. also for description of various diffusion pumps: S. Dushman, *op. cit.*; L. Dunoyer, *Vacuum Practice*, trans. by J. H. Smith (New York: D. Van Nostrand and Co., Inc., 1928).

mixture diffuse at different rates into the flowing gas (due to their differing diffusion coefficients) and therefore a partial separation is effected.<sup>4</sup>

(45) **Thermal Diffusion. Definition and Qualitative Argument:** Enskog,<sup>1</sup> and independently Chapman,<sup>2</sup> discovered theoretically that a temperature gradient should give rise in a gas mixture to a diffusion, partially separating the components. In liquids, this has long been known as the Soret effect. In gases, a special case, namely, one in which one kind of the molecules consists of particles of very large mass and size compared to the other kind, has already been treated when the motion of particles in a thermal gradient was considered<sup>3</sup> (Section 37).

In general, however, the theory is very complicated.<sup>4</sup> The effect can be found through a more exact calculation of the function  $\Phi_1$  in (16.9). The result is that the expression for the normal diffusion has to be modified. For the flow in the  $z$ -direction of the molecules of kind 1 we may write<sup>5</sup> (compare [43.1])

$$-D \frac{\partial c_1}{\partial z} \quad (45.1)$$

As long as the total concentration ( $c_1 + c_2$ ) is constant, this is identical with

$$-D(c_1 + c_2) \frac{\partial}{\partial z} \left( \frac{c_1}{c_1 + c_2} \right) \quad (45.2)$$

Now, however, due to the temperature gradient,  $c_1 + c_2$  varies in a manner proportional to  $1/T$ . Obviously (45.2) is to be used, as otherwise we would be led to speak of diffusion in a simple gas ( $c_2 = 0$ ) in a temperature gradient. We will call

$$\frac{c_1}{(c_1 + c_2)} = x \quad \frac{c_2}{(c_1 + c_2)} = 1 - x \quad (45.3)$$

where  $x$  is the mole fraction of the first component. Then the flow of the first component through 1 cm<sup>2</sup>/sec is to be written

$$\begin{aligned} -D(c_1 + c_2) \frac{\partial x}{\partial z} - D_T \frac{(c_1 + c_2)}{T} \frac{\partial T}{\partial z} \\ = -D(c_1 + c_2) \left( \frac{\partial x}{\partial z} + k_T \frac{\partial \ln T}{\partial z} \right) \end{aligned} \quad (45.4)$$

<sup>4</sup> G. Hertz, *Physik. Z.*, **23**, 433 (1922); *Z. Physik*, **91**, 810 (1934); R. Sherr, *J. Chem. Phys.*, **6**, 251 (1938); F. A. Schwerts, *Amer. J. Physics*, **15**, 31 (1947). Theory: A. von Hartel, N. Meer, and M. Polanyi, *Z. phys. Chem.*, **B**, **19**, 145 (1932); H. Barwich, *Z. Physik*, **100**, 166 (1936); D. MacGillivray, *Trans. Faraday Soc.*, **33**, 433 (1937); *Rec. Trav. Chim.*, **56**, 330 (1937); E. Blumenthal, *Phil. Mag.*, **27**, 341 (1939).

<sup>1</sup> *Physik. Z.*, **12**, 538 (1911); *Ann. Physik*, **38**, 742 (1912).

<sup>2</sup> *Phil. Trans. Roy. Soc.*, **217**, 157 (1937); S. Chapman and F. W. Dootson, *Phil. Mag.*, **33**, 268 (1917).

<sup>3</sup> T. L. Ibbs, *Trans. Faraday Soc.*, **32**, 1082 (1933).

<sup>4</sup> S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-uniform Gases* (London: Cambridge University Press, 1939).

<sup>5</sup> We are using here the subscripts 1 and 2, instead of unprimed and primed quantities.

where  $D_T$  is the coefficient of thermal diffusion and  $k_T$  is defined as

$$k_T = \frac{D_T}{D} \quad (45.5)$$

In the stationary state for a closed vessel

$$\frac{\partial x}{\partial z} = -k_T \frac{\partial \ln T}{\partial z} \quad (45.6)$$

In the case of elastic molecules (in general, in the case of molecules which repel each other with a law of force in which the exponent is more negative than  $-5$ ) the heavier gas moves in the direction of the gradient.

Besides the thermal diffusion ratio  $k_T$ , Chapman introduces also the thermal diffusion factor  $\alpha$ , defined by

$$\alpha x(1-x) = k_T \quad (45.7)$$

Frankel<sup>6</sup> has applied the ideas of Stefan (Section 42) to investigate the dependence of thermal diffusion on the force law. His arguments have been elaborated by Cacciapuoti<sup>7</sup> for rigid molecules and presented in detail by Furry,<sup>8</sup> whom we follow here. The question is then this: Assume a uniform mixture of two gases; a temperature gradient in the  $z$ -direction is now established. What force do the two gases exert on each other, or in other words, what linear momentum does one gas transfer to the other in the  $z$ -direction? It becomes immediately clear that for Maxwellian molecules thermal diffusion is absent. According to Equation (42.35) the momentum transfer between the two gases is independent of the molecular velocity and is, therefore, not affected by the existence of a temperature gradient.

Consider next molecules harder than Maxwellian ones, i.e., with  $s$  larger than 4. (This is the case for all neutral molecules; rigid molecules correspond to  $s = \infty$ .) In this case the effect of fast molecules in transferring momentum is greater and, consequently, their number more important. If a temperature gradient exists in a mixture of gases of different molecular weight, the average velocity of the lighter gas molecules coming from the hot region is more increased than the velocity of the heavier molecules coming from the hot region. Therefore,<sup>9</sup> on the average, the light gas transfers to the heavy gas momentum in the direction opposite to the temperature gradient, i.e., the heavier gas is pushed toward the cold part, the lighter gas toward the hot part. The effect, being due to a momentum transfer, should be proportional to the product of the mole fractions. If the molecules were "softer" than Maxwellian molecules, the sign of the effect would be in the opposite direction.

If the masses are equal but the effective diameter different for the two gases, the smaller molecules, which have the greater mean free path, will come

<sup>6</sup> *Phys. Rev.*, 57, 661 (1940).

<sup>7</sup> *Nuovo Cimento*, 1, 126 (1943).

<sup>8</sup> *Amer. J. Physics*, 16, 63 (1948).

<sup>9</sup> In the momentum transfer only the effective mass  $\bar{m}$  appears explicitly.

from farther away than the larger molecules. Therefore, among the molecules coming from the hot region, the smaller molecules will carry comparatively a larger excess of velocity than the bigger molecules. If the molecules are harder than Maxwellian molecules the result is therefore that the bigger molecules will be pushed toward the cold side; hence, the smaller molecules will accumulate at the hot side, the bigger molecules at the cold side.

It should be emphasized here that thermal diffusion is much more sensitive to the details of the law of interaction than the transport quantities discussed in earlier sections. For the latter, the law of interaction determines mainly the temperature dependence, while even the sign of thermal diffusion depends on the law of interaction.

**(46) Thermal Diffusion. Approximate Calculations:** We proceed next in the following manner, according to Furry, to get a formula for  $D_T$ . Consider the stationary case, in which there is no flow. Then, in analogy to the considerations of Stefan, the force due to the gradient of the partial pressure of gas 1 to gas 2 because of the temperature gradient. According to (45.6), this momentum is therefore equal to  $-(c_1 + c_2)kTR(\partial T/\partial x)$ . To calculate the momentum transfer according to (42.38), we assume approximate distribution functions  $f_1$  and  $f_2$  (called  $f$  and  $f'$  in [42.38]). This is done by combining Equations (37.2), (37.7) and (37.9)

$$f_1 = N_A c_1 \left( \frac{m_1}{2\pi kT} \right)^{\frac{3}{2}} e^{-\frac{m_1 w^2}{2kT}} \left[ 1 - \left( \frac{m_1}{2kT} \right)^{\frac{1}{2}} \zeta \left( 1 - \frac{2m_1 w^2}{5kT} \right) \Lambda_1 a_1 \frac{1}{T} \frac{\partial T}{\partial z} \right] \quad (46.1)$$

By assuming  $a_1$  and  $a_2$  to have the same values as if the other gas were absent, effects which might be appreciable are neglected. Inserting into (42.38) and integrating, we find for the momentum transferred (see Equation [42.23])

$$(c_1 + c_2)RT \frac{\partial x}{\partial z} = -x(1-x)\bar{m}^2 \frac{32}{3} p^2 (2kT)^{-\frac{1}{2}} \cdot \frac{1}{T} \frac{\partial T}{\partial z} (\Lambda_1 a_1 m_1^{-\frac{1}{2}} - \Lambda_2 a_2 m_2^{-\frac{1}{2}}) (\Omega_{12}^{(1)}(1) - \Omega_{12}^{(1)}(2)) \quad (46.2)$$

where the integrals  $\Omega$  have been defined in Equation (17.7).

Other approximate derivations have been given by R. Fürth,<sup>1</sup> and by Rai and Kothari.<sup>2</sup> Gillespie<sup>3</sup> has proposed an explanation of thermal diffusion similar to that used by Maxwell in the treatment of thermal pressure differences in wide tubes (Section 35). The molecular flow considerations show that a temperature gradient should produce a thermal flow of the first component

$$2\Lambda \frac{\partial}{\partial z} (c_1 w_1)$$

<sup>1</sup> *Proc. Roy. Soc., A*, 179, 461 (1942).

<sup>2</sup> *Indian J. Phys.*, 17, 103 (1943).

<sup>3</sup> *J. Chem. Phys.*, 7, 531 (1939); see also J. W. Westhaver and A. K. Brewer, *ibid.*, 8, 314 (1940).

To have no net flow in the stationary state, a counter flow  $W$  must be superimposed over the whole gas. This carries

$$\frac{c_1}{c_1 + c_2} W$$

of the first component, and so

$$2\Lambda \frac{\partial(c_1 w_1)}{\partial z} = \frac{c_1}{c_1 + c_2} W \quad (46.3)$$

A similar equation must also hold for the second component. Taking  $\Lambda$  equal for both

$$\frac{1}{c_1} d(c_1 w_1) = \frac{1}{c_2} d(c_1 w_2) \quad (46.4)$$

and, as  $w \propto T^{\frac{1}{2}} m^{-\frac{1}{2}}$ ,

$$\frac{1}{c_1 \sqrt{m_1}} d(c_1 \sqrt{T}) = \frac{1}{c_2 \sqrt{m_2}} d(c_2 \sqrt{T}) \quad (46.5)$$

or, as  $c_1 + c_2$  is inversely proportional to  $T$ ,

$$\frac{T}{x} d\left(\frac{x}{\sqrt{T}}\right) = \sqrt{\frac{m_1}{m_2}} \frac{T}{1-x} d\left(\frac{1-x}{\sqrt{T}}\right) \quad (46.6)$$

Therefore

$$-\frac{dx}{dT} = k_T = \frac{1}{2} x(1-x) T \frac{\sqrt{m_1} - \sqrt{m_2}}{x\sqrt{m_1} + (1-x)\sqrt{m_2}} \quad (46.7)$$

This shows qualitative agreement with experiment.

(47) **Thermal Diffusion. Exact Theory:** The exact theory of thermal diffusion can be found in Chapman and Cowling's book;<sup>1</sup> it is rather formidable, and only the first approximation will be presented here. In the main, our notation follows this book; exceptions will be noted.<sup>2</sup>

We introduce the mass ratio

$$\left. \begin{aligned} \mu &= m_1/(m_1 + m_2) && \text{(called } M_1 \text{ in C. C.)} \\ 1 - \mu &= m_2/(m_1 + m_2) && \text{(called } M_2 \text{ in C. C.)} \end{aligned} \right\} \quad (47.1)$$

and

$$\Delta = (m_1 - m_2)/(m_1 + m_2)$$

The mole fraction  $x$  is called  $n_{10}$  in C. C.,  $1 - x$  is written  $n_{20}$ . Then the following functions (of  $T$  and the force law) are defined (C. C., p. 164):

$$\left. \begin{aligned} A &= \frac{1}{5} \Omega_{12}^{(2)}(2) / \Omega_{12}^{(1)}(1) \\ B &= [\Omega_{12}^{(1)}(2) - \frac{1}{5} \Omega_{12}^{(1)}(3)] / \Omega_{12}^{(1)}(1) \\ C &= \frac{2}{5} \Omega_{12}^{(1)}(2) / \Omega_{12}^{(1)}(1) \\ e &= kT / [8\mu(1 - \mu) \Omega_{12}^{(1)}(1)] \end{aligned} \right\} \quad \text{(called } E \text{ by C. C.)} \quad (47.2)$$

<sup>1</sup> Chapman and Cowling, subsequently referred to as C. C. Sections 47 and 48 are essentially abstracts from this book supplemented by more recent literature.

<sup>2</sup> In earlier papers of Chapman different notations were used.



These appear in the following combinations:

$$s_1 = \frac{\mu^2 e}{\eta_1} - (1 - \mu)(-3\Delta + 4\mu A) \quad (47.3)$$

$$s_2 = \frac{(1 - \mu)^2 e}{\eta_2} - \mu(3\Delta + 4(1 - \mu)A)$$

$$q_1 = \frac{\mu e}{\eta_1} [6(1 - \mu)^2 + 5\mu^2 - 4\mu^2 B + 8\mu(1 - \mu)A]$$

$$q_2 = \frac{(1 - \mu)e}{\eta_2} [6\mu^2 + 5(1 - \mu)^2 - 4(1 - \mu)^2 B + 8\mu(1 - \mu)A] \quad (47.4)$$

$$q_{12} = 3\Delta^2(5 - 4B) + 4\mu(1 - \mu)A(11 - 4B) + 2\mu(1 - \mu) \frac{\nu}{\eta_1 \eta_2}$$

( $q_1$ ,  $q_2$ ,  $q_{12}$  are called  $Q_1$ ,  $Q_2$ , and  $Q_{12}$  in C. C., p. 164)

It is then found that (C. C., p. 167)

$$k_T = x(1 - x)5(C - 1) \frac{s_1 x - s_2(1 - x)}{q_1 x^2 + q_2(1 - x)^2 + q_{12}x(1 - x)} \quad (47.5)$$

A positive  $k_T$  means that gas 2 accumulates in the hotter portions of the vessel.

Chapman<sup>3</sup> has discussed the dependence of  $k_T$  on the mole fraction  $x$ . If  $\alpha$  is independent of  $x$ ,  $k_T$  has a maximum at  $x = \frac{1}{2}$  and is symmetric around this point. But dependent on the pair of gases selected, the maximum might be shifted to one side. In the most general case the curve might have, at either or both ends, i.e., at  $x = 0$  and  $x = 1$ , a positive, zero, or negative tangent, and  $k_T$  may change sign at a certain mole fraction.

For such a change of sign to occur,  $\Delta$  must be small and the heavier molecules must have the smaller diameter. Then  $s_1$  and  $s_2$  have the same sign and the change of signs for  $k_T$  occurs at the mole fraction (see [47.5])

$$\frac{x}{(1 - x)} = \frac{s_2}{s_1} \quad (47.6)$$

Grew<sup>4</sup> has found that for Ne-NH<sub>3</sub> mixtures,  $k_T$  is negative between 0 and 75 per cent Ne, positive above 75 per cent Ne. This change seems however rare; it does not occur, for example, in A-HCl or N<sub>2</sub>O-CO<sub>2</sub> mixtures.

If gas 2 is present only in small amount,  $1 - x$  is small,  $x$  close to unity, and Equation (47.5) takes the form

$$k_T = 5(C - 1) \frac{s_1}{q_1} (1 - x) \quad (47.7)$$

<sup>3</sup> *Proc. Roy. Soc., A*, 177, 38 (1940).

<sup>4</sup> *Phil. Mag.*, 35, 30 (1944).

For molecules with exactly the same force law and effective diameter but different mass (isotopes), Equation (47.5) can be developed into powers of  $\Delta$ ; the result, including the second power of  $\Delta$ , but with no restrictions as to  $x$  is <sup>5</sup>

$$k_T = 3(5C - 1) \frac{(A + 1)}{A} (11 + 8A - 4B)^{-1} \Delta \cdot x(1 - x) \\ \times \left\{ 1 - \left[ \frac{3}{4} \cdot \frac{(2 - A)}{(1 + A)} - \frac{(2 + 8B)}{(11 + 8A - 4B)} \right] \Delta \cdot (2x - 1) \right\} \quad (47.8)$$

In case the masses are very unequal, molecule 1 may be taken as the heavy one,  $m_1 \gg m_2$ , and then  $\mu = 1$ ,  $1 - \mu = 0$ . Taking account of the relation (C. C., p. 165)

$$D = \frac{3e}{2(M_1 + M_2)} \frac{RT}{p} \quad (47.9)$$

which follows from (42.39) and (47.2), expressions (47.3) and (47.4) take the form

$$s_1 = \frac{e}{\eta_1} = 2(M_1 + M_2) \frac{p}{RT} \frac{D}{3\eta_1}, \quad -3 \quad (47.10)$$

$$q_1 = (5 - 4B) \frac{\gamma}{\eta_1} \quad q_2 = 6(1 - \mu) \frac{\gamma}{\eta_2} \quad (47.11)$$

$$q_{12} = 3(5 - 4B) + 2(1 - \mu) \frac{\gamma}{\eta_1 \eta_2}$$

If the light gas is present in small quantities only,  $x \sim 1$  and (see [47.7])

$$\alpha = \frac{5(C - 1)}{(5 - 4B)} \quad (47.12)$$

If the heavy gas is present in small quantities only,  $x$  is small, and

$$\alpha = -5(C - 1) \frac{s_2}{q_2} = \frac{15}{4} (C - 1) \frac{RT}{pM_2} \frac{\eta_2}{D} \quad (47.13)$$

To see how good the first approximation (47.5) is, Jones has compared it in the case of a Lorentz gas (electrons), for which the molecules <sup>6</sup> have very great mass and are distributed according to the Maxwell distribution function. The difference is found to be 0 to 25 per cent, depending on the force law. C. C., p. 196, give as ratio of  $k_T$ , calculated according to (47.5), to the exact value, for  $s = \infty$  (hard molecules): 0.77;  $s = 12$ : 0.85;  $s = 8$ : 0.89.

<sup>5</sup> Chapman, *loc. cit.*, p. 57. In this paper, Chapman gives also a detailed discussion of the dependence of  $k_T$  on the nature of the two gases.

<sup>6</sup> R. C. Jones, *Phys. Rev.*, 58, 111 (1940); 59, 1019 (1941).

Waldmann<sup>7</sup> had considered quantum theoretical effects in thermal diffusion, like the effect of the spin and of the rotational state (see analogous considerations in the case of viscosity, section 22).

(48) **Special Models. Rigid Sphere Model:**<sup>1</sup> For the rigid sphere model there follows

$$A = \frac{2}{5} \quad B = \frac{3}{5} \quad C = \frac{6}{5} \quad (48.1)$$

$$\frac{e}{\eta_1} = \frac{4}{5} \cdot \frac{1}{\mu \sqrt{2(1-\mu)}} \frac{d_1^2}{d_{12}^2} \quad \frac{e}{\eta_2} = \frac{4}{5} \frac{1}{(1-\mu) \sqrt{2\mu}} \frac{d_2^2}{d_{12}^2} \quad (48.2)$$

$$\frac{d_1^2}{d_{12}^2} = 4 \left[ 1 + \sqrt{\frac{(1-\mu)\eta_1}{\mu\eta_2}} \right]^{-1} \quad (48.3)$$

$$s_1 = \frac{4}{5} \frac{\mu}{\sqrt{2(1-\mu)}} \frac{d_1^2}{d_{12}^2} - (1-\mu) \left( -3\Delta + \frac{8}{5}\mu \right) \quad (48.4)$$

$$s_2 = \frac{4}{5} \frac{(1-\mu)}{\sqrt{2\mu}} \frac{d_2^2}{d_{12}^2} - \mu \left( 3\Delta + \frac{8}{5}(1-\mu) \right)$$

$$q_1 = \frac{24}{5} [2(1-\mu)]^{-\frac{1}{2}} \frac{d_1^2}{d_{12}^2} \left[ 1 - \frac{22}{15}\mu + \frac{9}{10}\mu^2 \right] \quad (48.5)$$

$$q_2 = \frac{24}{5} [2\mu]^{-\frac{1}{2}} \frac{d_2^2}{d_{12}^2} \left[ 1 - \frac{22}{15}(1-\mu) + \frac{9}{10}(1-\mu)^2 \right]$$

$$q_{12} = \frac{39}{5} \Delta^2 + \frac{344}{25} \mu(1-\mu) + \frac{16}{25} [\mu(1-\mu)]^{-\frac{1}{2}} \frac{d_1^2 d_2^2}{d_{12}^4}$$

This can be further specialized to two cases.

(a) *Molecules of Equal Mass:*  $m_1 = m_2$ ;  $\mu = 1 - \mu = \frac{1}{2}$ .

$$s_1 = \frac{2}{5} \left( \frac{d_1^2}{d_{12}^2} - 1 \right); \quad s_2 = \frac{2}{5} \left( \frac{d_2^2}{d_{12}^2} - 1 \right) \quad (48.6)$$

$$q_1 = \frac{59}{25} \frac{d_1^2}{d_{12}^2}; \quad q_2 = \frac{59}{25} \frac{d_2^2}{d_{12}^2} \quad (48.7)$$

$$q_{12} = \frac{86}{25} + \frac{32}{25} \cdot \frac{d_1^2 d_2^2}{d_{12}^4}$$

This case has been investigated by Wall and Holley<sup>2</sup> for the pairs CO<sub>2</sub> - C<sub>3</sub>H<sub>8</sub>; N<sub>2</sub>O - C<sub>3</sub>H<sub>8</sub>; CO - C<sub>2</sub>H<sub>4</sub>; CO - C<sub>2</sub>H<sub>6</sub>; N<sub>2</sub> - C<sub>2</sub>H<sub>4</sub>; CO<sub>2</sub> - N<sub>2</sub>O; CO - N<sub>2</sub>. For the last pair,  $\alpha$  is negligible both according to theory and experiment; for CO<sub>2</sub> - N<sub>2</sub>O, the experimental value is about 10 times the theoretical value; for all other pairs, the theoretical value is 2 to 4 times the experimental one.

<sup>7</sup> *Z. Naturf.*, 1, 483 (1946).

<sup>1</sup> C. C., Chapter X.

<sup>2</sup> *J. Chem. Phys.*, 8, 949 (1940).

Chapman has suggested that, for molecules which are not quite hard spheres, Equations (48.1), (48.2), (48.4) and (48.5) may still be used, provided  $d_1^2/d_{12}^2$  is defined by (48.3).

(b) *Isotopes*:  $d_1 = d_2 = d_{12}$ . For the general case, there is no need to write again the equations which follow from (48.1) to (48.5). In the case in which  $\Delta$  is small, (48.7) takes the form

$$k_T = x(1 - x) \frac{105}{118} \Delta [1 - 0.281\Delta(2x - 1)] \quad (48.8)$$

The quantity preceding the brackets was first given by Furry, Jones and Onsager.<sup>3</sup> According to the rigid sphere model,  $k_T$  should be independent of the temperature.

(49) **Special Models. Interaction Through Central Forces**: Assume first that the mutual potential energy of the molecules is given by

$$Kr^{-s} \quad (49.1)$$

and that both  $K$  and  $s$  are the same for the interaction of molecules 1 and 2 as for interaction of molecules of the same kind. Then

$$A = \frac{1}{5} \left( 3 - \frac{2}{s} \right) \frac{A_2}{A_1}, \quad B = \frac{1}{5} \left( 3 - \frac{2}{s} \right) \left( 1 + \frac{2}{s} \right), \quad (49.2)$$

$$\frac{2}{5} \left( 3 - \frac{2}{s} \right), \quad \frac{e}{\eta_1} = \frac{2}{5\mu} [2(1 - \mu)]^{-\frac{1}{2}} \left( 3 - \frac{2}{s} \right) \frac{A_2}{A_1}$$

$A_2$  and  $A_1$  are numbers depending on  $s$ ; the value of  $A_2/A_1$  is shown in Table X.

TABLE X  
SOME CONSTANTS OF IMPORTANCE IN THERMAL DIFFUSION

$s + 1 (= \nu)$	3	5	7	9	11	15	$\infty$
$A_2/A_1$ (49.2)	1.499	1.033	0.925	0.868	0.831	0.787	0.667
$C$ (49.3)	0.714	0.8156	0.8431	0.8648	0.8823	0.9064	1.000
$F$ (49.5)	0.4824	0.3831	0.3275	0.2900	—	—	—
$H$ (49.7)	0.000	0.833	0.557	0.293	0.120	-0.0833	-0.482

It follows from the preceding that, in this case too, all the quantities entering  $k_T$  and, therefore, this quantity itself, are independent of  $T$ . If the exponent in (49.1) is different for the interaction between molecules 1 and 2 and interaction between two molecules 1,  $e/\eta_1$  contains a factor  $T$  with the exponent  $(2/s_{12}) - (2/s_{11})$ .

<sup>3</sup> *Phys. Rev.*, **55**, 1083 (1939).

<sup>1</sup> C. C., p. 170, use  $\nu = s + 1$ .

For isotopes of nearly equal mass, a quantity  $R_T$  is introduced, defined as the ratio of the actual  $k_T$  to that value which Equation (48.8) would give for hard molecules with the same masses as the actual molecules.

Jones<sup>2</sup> has shown that, for the model just discussed,

$$R_T = \left(1 - \frac{4}{s}\right) C(s+1) \quad (49.3)$$

where  $C(s+1)$  is a pure number, given in Table X. Equation (49.3) shows the absence of thermal diffusion in Maxwellian molecules ( $s = 4$ ), as discussed earlier (Section 46). Between  $s = 4$  and  $s = \infty$  (hard spheres),  $R_T$  rises monotonously from zero to unity.

Brown<sup>3</sup> suggested the use of (49.3), omitting  $C$ , while determining the  $s$ -value from the temperature variation of the viscosity ( $T^{1-2/s}$ , see discussion following (21.12)). Good agreement is found, except for the carbon isotopes in methane.

For the Sutherland model of a hard sphere of collision diameter  $d_{12}$ , with an attractive mutual potential of the form

$$\epsilon = -\epsilon_0 \left(\frac{d_{12}}{2r}\right)^s \quad (49.4)$$

where  $-\epsilon_0$  is the potential energy on contact, Jones<sup>4</sup> found

$$R_T = 1 - \frac{\epsilon_0}{kT} F(s+1) \quad (49.5)$$

where the numbers  $F$  are given in Table X. It is evident from (49.5) that the values are temperature dependent. This is also the case for the Lennard-Jones model which assumes an interaction of the form

$$\epsilon = -K'r^{-s'} + Kr^{-s} \quad (49.6)$$

The exact expression for this case has not been given in general in closed form. For  $s' = 2$ , we have

$$R_T = C(s+1) \left[1 - \frac{4}{s} + H(s+1) \left(\frac{\epsilon_0}{kT}\right)^{1-2/s}\right] \quad (49.7)$$

The number  $H(s+1)$  is also given in Table X, while  $\epsilon_0$  is the energy at the minimum of the potential (49.6), i.e.,

$$\epsilon_0 = (1 - \sigma)K' \left(\frac{\sigma K'}{K}\right)^{\sigma/(1-\sigma)} \quad \text{with} \quad \sigma = \frac{s'}{s} \quad (49.8)$$

For  $s' = 4$  and  $s = 8$ , R. C. Jones has made a numerical calculation, with the following results: For infinite  $T$ ,  $R_T$  starts at about 0.43, rises to about 0.48

<sup>2</sup> *Phys. Rev.*, **58**, 111 (1940).

<sup>3</sup> *Ibid.*, **57**, 242 (1940).

<sup>4</sup> *Ibid.*, **59**, 1019 (1941).

at  $\epsilon_0/kT = 0.04$ , then falls gradually to zero around  $\epsilon_0/kT = 0.55$ , goes to a minimum equal to  $-0.63$  at  $\epsilon_0/kT = 2.25$ , rises again and approaches zero asymptotically.

For the case of the general Lennard-Jones potential (49.6), R. C. Jones finds approximately

$$R_T \quad C(s+1) \left[ 1 - \frac{4}{s} + \frac{8\sigma}{s} \left( \frac{1}{2\sigma} - 1 \right)^\sigma \left( \frac{\epsilon_0}{kT} \right)^{1-\sigma} \right] \quad (49.9)$$

For the Lennard-Jones interaction energy (49.6) with  $s' = 6$ ,  $s = 12$ , Hirschfelder and his coworkers<sup>5</sup> have tabulated the quantities  $A$ ,  $B$ , and  $C$  defined in (47.2) and also a function  $W'(1)$  from which  $e$  can easily be calculated.

(50) **Experimental Results for Thermal Diffusion:** The experimental tests of the preceding formulas have, in general, two aims: The determination of  $s$  (the exponent in the mutual potential energy) from the absolute value of  $R_T$ , and the measurement of the temperature dependence. Some of the earlier papers are not reliable, since they use incorrect formulas, e.g., omitting the factor  $C$  in (49.3).

Harrison and Hirst<sup>1</sup> have used formulas for radon-helium and radon-hydrogen mixtures in which the partners have very different masses, and with the help of Equations (47.13), find  $s = 5.45$  for He-radon,  $s = 5$  for He-H<sub>2</sub>.

TABLE XI  
 $R_T$  FOR PAIRS OF RARE GASES

Mixture	He-Ne	He-A	He-X	Ne-A	A-X
ABI <sup>2</sup> .....	0.80	0.63	0.62	0.55	0.17
Grew <sup>3</sup> -156°C.....	0.58	0.55	—	0.28	—
- 88°C.....	0.63	0.61	0.66	0.44	0.13
20°C.....	0.64	0.64	0.66	0.52	0.18
191°C.....	0.64	0.66	0.66	0.57	0.37
312°C.....	0.64	0.66	0.66	0.57	0.45

IBBS<sup>2</sup> and his collaborators, and Grew<sup>3</sup> have measured pairs of rare gases. Table XI shows some of the results. From the measurements at room temperature, Grew concludes to an  $s$ -value of 9.5–10.2. Measurements on CO<sub>2</sub> and N<sub>2</sub>O which show a discontinuity are still disputed.<sup>4</sup>

<sup>5</sup> J. O. Hirschfelder, R. B. Bird and E. L. Spotz, *J. Chem. Phys.*, **16**, 968 (1948). Table IV gives  $A$ ,  $B$ ,  $C$ , Table I  $W'(1)$ .

<sup>1</sup> G. E. Harrison, *Proc. Roy. Soc., A*, **161**, 80 (1937); W. Hirst and G. E. Harrison, *ibid.*, **169**, 573 (1939).

<sup>2</sup> B. E. Atkins, R. E. Bastick, and T. L. Ibbs, *ibid.*, **172**, 142 (1939); *see also*, M. Puschner, *Z. Physik*, **106**, 597 (1937).

<sup>3</sup> *Proc. Roy. Soc., A*, **189**, 402 (1947).

<sup>4</sup> T. L. Ibbs and A. C. R. Wakeman, *ibid.*, **134**, 613 (1932); R. E. Bastick, H. R. Heath, and T. L. Ibbs, *ibid.*, **173**, 543 (1939); G. and O. Blüh, *Z. Physik*, **90**, 12 (1934); G. and O. Blüh and M. Puschner, *Phil. Mag.*, **24**, 1103 (1937).

Heath, Ibbs, and Wild <sup>5</sup> have found  $R_T = 0.61$  in  $H_2-D_2$  mixtures, from which they conclude  $s = 10.6$ ; as a function of the deuterium content,  $R_T$  should vary theoretically from 0.60 (10 per cent)  $D_2$  to a maximum of 0.633 at 75 per cent  $D_2$ , falling to 0.626 for 90 per cent  $D_2$ . The experiments seem to be in agreement with these calculations.

As far as the temperature dependence is concerned, use of the Clusius column, with its large temperature difference, raises the question as to what  $T$  the thermal diffusion ratio, found experimentally, is to be assigned. Brown <sup>6</sup> shows that the correct temperature is

$$T_r = \frac{T_1 T_2}{(T_2 - T_1)} \ln \frac{T_2}{T_1} \quad (50.1)$$

where  $T_2$  is the temperature of the hot wire and  $T_1$  that of the cool wall.

As mentioned in Section 49, the assumption of a repulsive potential proportional to an inverse power of the distance leads to an  $R_T$  independent of the temperature. Experimentally however (see e.g., Table XI),  $R_T$  is lower at lower temperatures. As mentioned earlier  $R_T$  increases with  $s$ , so that the previous results can be expressed by saying that the molecules are less hard (have smaller  $s$ ) the lower the average velocity of the molecules (the lower the temperature), i.e., the less they approach each other. Another interpretation (which is not really different) is to assume attractive forces also.

Grew <sup>7</sup> has pointed out that for certain mixtures (e.g., Ne-A) the curve of  $R_T$  as function of  $\epsilon_0/kT$  has a form closely paralleling the theoretical curve for a Lennard-Jones model with  $s' = 4$ ,  $s = 8$ , although shifted both horizontally and vertically. For other pairs, the experimental curve flattens out too much at low temperatures; for isotopes (see Stier, below) it does not fit at all.

Stier <sup>8</sup> has measured the thermal diffusion of the argon and neon isotopes, and expressed empirically the temperature dependence of  $R_T$  in the following manner:

$$\text{A:} \quad R_T = 0.25 \ln \frac{T}{86.9} \quad (50.2)$$

$$\text{Ne:} \quad R_T = 0.25 \ln \frac{T}{26.6} \quad (50.3)$$

Similarly, Watson and Woernley <sup>9</sup> found, for a separation of  $^{14}\text{N}$  and  $^{16}\text{N}$  in  $\text{NH}_3$ ,

$$R_T = 1.9 \ln \frac{T}{293} \quad (50.4)$$

This implies a change of sign at  $T = 293$ .

<sup>5</sup> *Proc. Roy. Soc., A*, **178**, 380 (1941); see also, K. Grew, *ibid.*, p. 390.

<sup>6</sup> *Phys. Rev.*, **58**, 661 (1940).

<sup>7</sup> *Loc. cit.*, 1947.

<sup>8</sup> *Phys. Rev.*, **62**, 548 (1942).

<sup>9</sup> *Ibid.*, **63**, 181 (1943).

These equations seem to indicate that a change of the sign of  $R_T$  (and of  $\alpha$ ) occurs at low temperatures. In agreement with this, Waldmann<sup>10</sup> has found a change of sign of  $\alpha$  in several gas mixtures, by the use of the inverse effect (Section 52). His results are shown in Table XII. A positive  $\alpha$  in this table means that the heavier gas moves toward the cooler region.

TABLE XII  
 $\alpha$  AS FUNCTION OF  $T$

	N <sub>2</sub> -A	O <sub>2</sub> -A	N <sub>2</sub> -O <sub>2</sub>
293°K. ....	0.07	0.051	0.018
89°K. ....	-0.022	-0.034	< -0.001

Van Itterbeek and his coworkers<sup>11</sup> have investigated  $k_T$  for a number of s, H<sub>2</sub>-O<sub>2</sub>, H<sub>2</sub>-N<sub>2</sub>, H<sub>2</sub>-CO, H<sub>2</sub>-Ne, H<sub>2</sub>-He, He-Ne, partly to very low temperatures (actually they plot a quantity  $\Delta\gamma$  against  $\ln T_1/T_2$ ;  $k_T$  is the slope of the curve). They find a decrease of  $k_T$  with decreasing temperature, although not a change in sign.

TABLE XIII

Gas Mixture	He (53.8%)-Ne			He (51.2%)-Ne		
$T^\circ\text{K.}$ .....	585.2	233.2	117.2	585.2	233.2	117.2
$R_T$ calc. ....	0.71	0.70	0.68	0.73	0.71	0.63
$R_T$ exp. ....	0.64	0.64	0.58	0.66	0.63	0.55

Gas Mixture	Ne (51.2)-A			CH <sub>4</sub> -H <sub>2</sub>	O <sub>2</sub> -CO <sub>2</sub>	CO-CO <sub>2</sub>	C <sup>12</sup> H <sub>4</sub> -C <sup>13</sup> H <sub>4</sub>
$T^\circ\text{K.}$ .....	585.2	233.2	117.2	506	735	725	274
$R_T$ calc. ....	0.66	0.52	0.27	0.68	0.61	0.60	0.29
$R_T$ exp. ....	0.57	0.48	0.28	0.67	0.63	0.40	0.49

It must be said that practically all the discussions of this section make use of a law of molecular interaction which does not, in general, represent the facts, but which gives results in closed form. At present, due to Hirschfelder and his coworkers,<sup>12</sup> numerical constants and tables of temperature functions are available for a law of molecular interaction which approaches reality much more closely.

They have numerically evaluated the constants in 47.3-47.5 and plotted  $k_T$  as a function of temperature and composition for mixtures of H<sub>2</sub> and D<sub>2</sub>.  $k_T$

<sup>10</sup> *Z. Naturf.*, **2a**, 358 (1947).

<sup>11</sup> A. van Itterbeek, O. van Paemel and J. van Lierde, *Physica*, **13**, 231 (1947).

<sup>12</sup> Footnote 13a, Section 42.



is positive at low and negative at high temperatures. (For experiments showing similar effects, see Table XII above.)

Table XIII shows a comparison between selected experimental data and Hirschfelder's calculation (which, as should be remembered, use constants found from viscosity and diffusion measurements). Other data are found in <sup>12</sup>.

(51) **Separation of Isotopes by Thermal Diffusion:**\* The idea of using thermal diffusion for the separation of isotopes was proposed by Chapman, but Mulliken<sup>1</sup> found it not to be promising. It became practical only when Clusius<sup>2</sup> connected it with the principles of reflux or fractionation, using as vehicle the convection currents set up when the temperature gradient is horizontal. Almost simultaneously, Brewer and Bramley<sup>3</sup> proposed a similar scheme. In a further publication Clusius and Dickel reported an experimental investigation on the influence of various factors, e.g., size of the tube, pressure, temperature difference, etc.

In the Clusius arrangement the gas is contained in a vertical or slightly inclined tube, the walls of which are at room temperature, while an electrically heated wire runs down the axis of the tube. It is possible to use instead two concentric tubes, the inner one being heated. The light gas accumulates at the top of the tube.

The theory of the process has been investigated independently by Furry, Jones and Onsager<sup>4</sup> and by Waldmann.<sup>5</sup> Instead of the cylindrical arrangement used experimentally they discuss one consisting of two parallel plates, because of the mathematical simplification.<sup>6</sup> This is, however, a good approximation to the case in which two concentric cylinders are used, with only a narrow space between. The notation adopted here is mainly that of Waldmann. He assumed a hot and a cold plate, distance  $d$  apart and height  $h$ . There is circulation of the gas, upward on the hot plate, downward on the cold plate. The details of the process at the top and at the bottom of the column, where the flow changes its direction by 180°, are neglected.<sup>7</sup> Calling the vertical coordinate  $z$  and that normal to the plate  $y$ , Waldmann writes the hydrodynamical equations.<sup>8</sup> They require first that the pressure is the same on every vertical cross-section, i.e., it is independent of  $y$ . There is, of course,

\* A very complete critical review by R. C. Jones and W. H. Furry is to be found in *Rev. Mod. Phys.*, **18**, 151 (1946). It was unfortunately not used when Section 51 was written.

<sup>1</sup> *J. Am. Chem. Soc.*, **44**, 1033 (1922).

<sup>2</sup> K. Clusius and G. Dickel, *Naturwiss.*, **26**, 546 (1938); *Z. phys. Chem.*, **B**, **44**, 397 (1939).

<sup>3</sup> *Science*, **90**, 165 (1938); *Phys. Rev.*, **55**, 590 A (1939).

<sup>4</sup> *Phys. Rev.*, **55**, 1083 (1939), referred to subsequently as F., J. and O.

<sup>5</sup> *Z. Physik*, **114**, 53 (1939).

<sup>6</sup> The calculations for the cylindrical case have been published by W. H. Furry and R. C. Jones, *Phys. Rev.*, **69**, 459 (1946).

<sup>7</sup> According to F., J. and O., the effect of the ends extends over a length

$$h' = \frac{d^4}{7536 M} \frac{C_p}{\rho^2} \frac{g}{\eta \lambda} \frac{\Delta T}{T_0} \sim \frac{d}{1728} \left( \frac{d}{\Lambda} \right)^2 \frac{M g d}{R T} \frac{\Delta T_0}{T_0},$$

therefore  $h$  must be taken much larger than  $2h'$ ,  $g$  being the acceleration of gravity.

<sup>8</sup> He calls  $x$  the direction which is here called  $y$ .

a variation of vertical speed across such a cross-section, as the flow varies from an upward direction on the hot plate to a downward flow on the cold side. The zero speed is present in the middle between the plates, if there is no resultant transport. If there is a resultant transport, i.e., untreated gas is admitted at the bottom, partially separated gas being withdrawn at the top, a constant upward velocity is superposed on the circulation, and the (vertical) sheet of zero flow is shifted toward the cold plate. The shearing stress resulting from the variation of speed over a horizontal cross-section, together with gravity, results in a vertical pressure gradient. In the case of no transport, it is found that

$$\overline{W} = \frac{1}{6} \frac{Mg}{z} \frac{p_0}{RT_0} \frac{\Delta T}{T_0} \frac{y}{d} (d - y) \left( y - \frac{d}{2} \right) \quad (51.1)$$

where  $T_0$ ,  $p_0$  are average values for temperature and pressure,  $\Delta T$  the temperature difference of the plates and  $g$  the acceleration of gravity.

Next the effect of diffusion is considered.<sup>9</sup> Waldmann finds then for the combined effect of diffusion, thermal diffusion and convection

$$-\frac{\partial}{\partial y} D \left[ \frac{\partial x}{\partial y} - \alpha x(1-x) \frac{\partial \ln T}{\partial y} \right] - D \frac{\partial^2 x}{\partial z^2} + W \frac{\partial x}{\partial z} = 0 \quad (51.2)$$

Here, the first term expresses horizontal diffusion, the second, thermal diffusion, the third, vertical diffusion, and the last, convection.<sup>10</sup> The solution is developed into a power series of  $\alpha$ , and the following results are obtained. Assume that  $x$  is kept  $x_0$  at the bottom and is  $x_0 + \Delta x_0$  at the top. Two characteristic lengths  $\bar{d}$  and  $\bar{h}$  are introduced by

$$\bar{d}^3 = 610 \frac{RT_0}{Mgp_0} \frac{T_0}{\Delta T} Dz \quad (51.3)$$

and

$$\frac{1.11}{\alpha} \cdot \frac{T_0}{\Delta T} \left[ \left( \frac{d}{\bar{d}} \right)^{-2} + \left( \frac{d}{\bar{d}} \right)^4 \right]; \quad (51.4)$$

If we assume  $h \ll \bar{h}$ , then, in the stationary state, in the absence of gas withdrawal,<sup>11</sup>

$$\Delta x = -x(1-x) \frac{h}{\bar{h}} = -x(1-x) \frac{\alpha}{1.11} \frac{\Delta T}{T_0} \frac{h}{d} \left( \frac{d}{\bar{d}} \right)^3 \left[ 1 + \left( \frac{d}{\bar{d}} \right)^6 \right]^{-1} \quad (51.5)$$

<sup>9</sup> P. Debye, *Ann. Physik*, **36**, 284 (1939), found that (51.5) is also valid in liquids provided  $\frac{Mg}{z} \frac{p_0}{RT_0} \frac{1}{T_0}$  in (51.3) is replaced by the more general expression: (density)  $\times$  (coefficient of thermal expansion).

<sup>10</sup> F., J. and O. first neglected lengthwise diffusion, then calculated it separately and added its effect.

<sup>11</sup> For large separations, the proper measure is the separation-factor, defined as the ratio of  $x/(1-x)$  at the top of the column to the value at the bottom.

If  $d > \bar{d}$ , then  $\Delta x \propto d^{-4}$  as found experimentally by Clusius and Dickel. There is a maximum at  $d = 0.89\bar{d}$ . For small  $d$ ,  $\Delta x \propto d^2$ . This behavior can be understood in a general way. If the distance is too small, viscosity prevents the setting up of strong convection currents. If the distance is too large, the thermal diffusion is too small. How essential the effect of the convection currents is, follows from the fact that the ratio of the  $\Delta x$  obtainable with and without convection is  $0.48h/\bar{d}$ .

The dependence of  $\Delta x$  on pressure comes in through the dependence on  $d/\bar{d}$  as  $D \propto p^{-1}$  and therefore  $\bar{d}^3 \propto p^{-2}$ . There exists an optimum pressure for a given  $d$ , namely, that pressure which makes  $d = 0.89\bar{d}$ .

Numerically, Waldmann used for air  $\alpha = 0.023$ ,  $D = 0.2 \text{ cm}^2/\text{sec}$ ,  $p_0 = 1 \text{ atm}$ ,  $T_0 = 400^\circ\text{K}$ ,  $\Delta T = 200^\circ$ ; then  $\bar{d} = 0.38$ , the best  $d$  is  $0.34 \text{ cm}$ , and the corresponding  $\bar{h}$  is  $68 \text{ cm}$ . All this applies to a simple, short tube, with  $h \ll \bar{h}$ . If the tube is long, but is subdivided at short intervals by gauze disks, it is found that (no transport,  $\alpha$  independent of  $T$ )

$$\frac{(1-x)}{x} = \frac{(1-x_0)}{x_0} e^{h/\bar{h}} \quad (51.6)$$

This relation of the dependence of separation on height seems to be well fulfilled in Clusius's experiments. F., J. and O. point out that an asymmetry in the temperature distribution sets up cross convection currents, which, by mixing the components, harm the efficiency of operation.

The exponent  $h/\bar{h}$  in (51.6) is equal, according to (51.3) and (51.4), to

$$\begin{aligned} \frac{h}{\bar{h}} &= \frac{\alpha}{1.11} \left( \frac{\Delta T}{T_0} \right)^2 \frac{h}{\bar{d}} \frac{\rho g}{610 D \eta} d^3 \left[ 1 + \left( \frac{1}{610} \cdot \frac{\Delta T}{T} \cdot \frac{\rho g d^3}{D \eta} \right)^2 \right]^{-1} \\ &= 550\alpha \frac{D \eta}{\rho g} \frac{h}{d^4} \left[ 372000 \left( \frac{D \eta}{\rho g d^3} \cdot \frac{T_0}{\Delta T} \right)^2 + 1 \right]^{-1} \end{aligned} \quad (51.7)$$

According to F., J. and O., the exponent in (51.6) is written  $2A_d h$ , which can be put into the form

$$2A_d h = 504\alpha f \frac{D \eta}{\rho g} \cdot \frac{h}{d^4} \left[ 363000 \left( \frac{D \eta}{\rho g d^3} \cdot \frac{T_0}{\Delta T} \right)^2 \frac{T_1^2 + T_1 T_2 + T_2^2}{3T_0^2} + 1 \right]^{-1}; \quad (51.8)$$

$f$  is a function of  $\Delta T/T$  but varies only between 1 for  $\Delta T = 0$  and 1.25 for  $(T_2/T_1) = \infty$ . Apart from the small difference in the coefficients (51.7) and (51.8) agree well, although F., J., and O. have assumed Maxwellian molecules ( $\Lambda$  proportional to  $T^{1/2}$ ).

For a long column without subdivision, F., J. and O. have expressed the dependence of composition on the height  $z$  within the column by

$$\begin{aligned} x &= \frac{1}{2} [1 + \tanh A(h-z)] \\ \tanh y &= \frac{(e^y - e^{-y})}{(e^y + e^{-y})} \end{aligned}$$

where  $A$ ,  $h_0$  are constants. This formula has been confirmed by Fleischmann.<sup>12</sup>

Nier<sup>13</sup> has tested the pressure dependence of the separating power of a column, as expressed in (51.7), (51.8). Evaluating (51.8) numerically for the separation of the C isotopes in methane, he calculated, with  $\alpha$  equal to 0.0077 (see also 51.6),

$$2A_d h \left( = \frac{h}{\bar{h}} \right) = \frac{2.19}{p^2} \left( 1 + \frac{0.25}{p^4} \right)^{-1} \quad (51.9)$$

where  $p$  is the pressure in atm. His experimental results can be represented by

$$2A_d h = \frac{2.19}{p^2} \left( 1.63 + \frac{0.208}{p^4} \right)^{-1} \quad (51.10)$$

The appearance of 1.63 instead of 1 in the denominator, which results in a decrease in efficiency, can be explained by a horizontal temperature difference (see above) of less than 5°C. Additional confirmation for a pressure dependence of the separating power of a column of the form of (51.9) has been given by Taylor and Glockler<sup>14</sup> and by Simon.<sup>15</sup>

For very large  $\Delta T$ , W. Groth<sup>16</sup> has found a decreased separation. This, according to Onsager and Watson<sup>17</sup>, is due to a change from laminar to turbulent flow. For thermal diffusion experiments, the Reynolds number is given by

$$[R] \quad 18\sqrt{3} \left( \frac{\rho}{\eta} \right)^2 \frac{T_2 - T_1}{T_2 + T_1} \quad (51.11)$$

and can therefore, for large  $\Delta T$ , exceed the critical value. Whether this has happened, can be recognized by measuring the heat loss from the inner cylinder as a function of  $p$ . As long as the flow is laminar, this loss is independent of  $p$ ; when the flow becomes turbulent, the heat loss increases greatly.

For a short tube, with an infinite reservoir at the bottom and a small reservoir, volume  $V$ , at the top, the process of establishing the stationary state is given by

$$\Delta x = -x(1-x) \frac{h}{\bar{h}} (1 - e^{-t/\tau}) \quad (51.12)$$

where

$$= \frac{hV}{q\bar{d}} \left[ 1 + \left( \frac{d}{\bar{d}} \right)^6 \right]^{-1} \quad (51.13)$$

and  $q$  is the cross-section of the tube. With air,  $V = 10^3 \text{ cm}^3$ ,  $q = 0.5 \text{ cm}^2$ ,  $l = 100 \text{ cm}$ ,  $\bar{d} = 0.4 \text{ cm}$ , Equation (51.13) gives  $\tau = 140$  hours.

<sup>12</sup> *Physik. Z.*, **41**, 14 (1940).

<sup>13</sup> *Phys. Rev.*, **57**, 30 (1940).

<sup>14</sup> *J. Chem. Phys.*, **8**, 843 (1940).

<sup>15</sup> *Phys. Rev.*, **69**, 596 (1946).

<sup>16</sup> *Naturwiss.*, **27**, 260 (1939).

<sup>17</sup> L. Onsager and W. W. Watson, *Phys. Rev.*, **56**, 474 (1939).

Bardeen<sup>18</sup> has extended the calculation to the case where it is intended to separate the heavier component, assumed to be present in small amounts only. His formula is rather complicated. The comparison with Waldmann's approximate Equations (51.12) and (51.13) shows fair agreement, if the proper value for the volume  $V$  of the reservoir at the top, which Waldmann assumed, is chosen. Comparison with Nier's measurements of the separation of  $^{13}\text{CH}_4$  in methane shows fairly good agreement (see Table XIV). All these develop-

TABLE XIV  
SEPARATION IN THERMAL DIFFUSION COLUMN

Hours.....	0	12	23	47	71
Experimental					
1 - $x$ bottom.....	0.0111	0.0202	0.0233	0.0248	0.0255
1 - $x$ top.....	0.0111	0.00615	0.00486	0.00404	0.00414
Separation factor.....	1.00	3.29	4.78	6.14	6.16
Theoretical					
Separation factor.....	1.0	3.5	5.0	6.1	6.2

ments are valid only beyond a certain time, which for gases is about an hour. For liquids, the time to reach equilibrium is much longer, because of the smaller value of  $D$ . Debye<sup>19</sup> recommended that the column be run for a time much shorter than that necessary for equilibrium, in which case much less separation would be effected. Under these conditions the performance of a column is independent of its length. It is true that the final separation increases very much with  $h$ , but so does the time to reach equilibrium. For a given duration  $t < \tau$ , the state is farther from equilibrium the longer the column, and these effects just compensate. For  $t = \frac{1}{2}\tau$ , the best performance is to be expected if  $(d/\bar{d})^3 = 2$ ; for  $t = 20\tau$  if  $(d/\bar{d})^3 = 4$ ;  $\tau$  is taken as  $h^2/\pi^2 D$ .<sup>20</sup>

Krasny-Ergen<sup>21</sup> has discussed theoretically the conditions for cheapest operation (power need) and construction of a separating column, if the amount and rate of the separation are prescribed. He finds, among other results, that the cost of single stage operation, where the cross-section of the column is constant, is 1.6 times that of multiple stage operation, where the cross-section of successive stages is smaller, according to the argument of Urey<sup>22</sup> and F., J. and O. (*loc. cit.*).

Of actually built separation columns, that of Nier has already been men-

<sup>18</sup> *Ibid.*, 57, 35 (1940).

<sup>19</sup> *Loc. cit.*

<sup>20</sup> Debye designates  $100(d/\bar{d})^3$  by  $g$ . For the stationary state, he finds optimum separation for  $g = 100$  or  $d = \bar{d}$ , instead of  $d = 0.89\bar{d}$  according to Waldmann.

<sup>21</sup> W. Krasny-Ergen, *Phys. Rev.*, 58, 1078 (1940).

<sup>22</sup> J. Wash. Acad. Sci., 30, 277 (1940); H. G. Thode and H. C. Urey, *J. Chem. Phys.*, 7, 34 (1939).

tioned. Watson<sup>23</sup> has constructed a multistage separation column and tested it on mixtures of  $N_2-CH_4$ , and on the isotope separation in neon and methane. A column for the separation of Cl isotopes has been described by Shrader.<sup>24</sup>

Taylor and Glockler<sup>25</sup> have built an apparatus containing 40 elements, each element with two concentric cylinders, the outer, cold one, a two-inch pipe of galvanized iron, the inner, hot one, a one-inch pipe. To be more exact, the annular free space is about 9 mm. With the inner tube at about 260°C, and 700 mm pressure, methane was used that contained about 1.3 per cent of  $^{13}CH_4$ . After 2 days, the concentration in the reservoir at the bottom was 2 per cent.

Seaborg, Wahl, and Kennedy<sup>26</sup> have used a column of 1 cm inner diameter and 7.5 m length, with an electrically heated molybdenum wire along the axis. For 1 atm and 250°C of the wire,  $H_2-D_2$  mixtures were tested. At equilibrium, which was reached after 3 days, 18 per cent  $D_2$  was found in the reservoir at the top (5 l volume), 87 per cent at the bottom of the column ( $\alpha = 30$ ). Other measurements were made with mixtures of deuterium and the radioactive isotope  $^3H$ . Although this was present in the mole fraction  $10^{-11}$ ,  $\alpha$  was found to be 5, which it should be, approximately, according to the value found for the previous mixture, taking into account the different masses involved. It follows that  $\alpha$  is substantially independent of  $x$ , as should be expected, contrary to some results of Clusius and Dickel who found an appreciable change when comparing chlorine mixtures where  $^{35}Cl:^{37}Cl$  varied from 7:3 to 2:3, with those where this ratio was between 1:8 and 1:150. In the same column, the separation factor for the  $^2H-^3H$  mixture was almost doubled by raising the temperature of the wire to 800°C.

A similar instrument was used by Kennedy and Seaborg<sup>27</sup> to separate chlorine isotopes (introduced as  $HCl$ ). After 6 days, the concentration of  $H^{35}Cl$  at the top was 95 per cent (wire temperature 650°C).

Bernstein and Taylor<sup>28</sup> have used the theory of the thermal diffusion column for consideration of a counter current column for isotope separation by chemical exchange.

(52) **The Inverse Thermal Diffusion Effect:** Dufour<sup>1</sup> took a vessel made of porous material, filled it with a gas 1, and plunged the porous vessel into another vessel filled with a lighter gas. The latter diffused more rapidly through the pores. Dufour found a temperature increase in the inner vessel; he interpreted this as due to the diffusion through the pores (see Section 35). However, from our present knowledge, it appears possible that the effect is due to diffusion within the inner vessel.

<sup>23</sup> *Phys. Rev.*, 57, 899 (1940).

<sup>24</sup> *Ibid.*, 69, 439 (1946).

<sup>25</sup> *J. Chem. Phys.*, 7, 851 (1939).

<sup>26</sup> *Ibid.*, 8, 639 (1940).

<sup>27</sup> *Phys. Rev.*, 57, 843 (1940).

<sup>28</sup> *J. Chem. Phys.*, 16, 903 (1948).

<sup>1</sup> *Arch. Sciences Phys. Nat.*, Geneva, 45, 9 (1872); *Pogg. Ann.*, 148, 490 (1873).

This latter effect was discovered (or rediscovered) by Waldmann.<sup>2</sup> However, the fundamental formula is given in Chapman and Cowling's book<sup>3</sup> although these authors have not made any use of it. It is found that the term (31.7) for the thermal flow has to be supplemented, so that the complete expression for the flow of heat is given, in the one dimensional case by

$$\begin{aligned} \text{Heat Flow} = & -\lambda \frac{\partial T}{\partial z} + \frac{5}{2}p[x(W_1 - W_M) + (1-x)(W_2 - W_M)] \\ & + p\alpha D \left( \frac{\partial x}{\partial z} + k_T \frac{1}{T} \frac{\partial T}{\partial z} \right) \quad (52.1) \end{aligned}$$

where  $W_M$  is the speed of the mass flow as given by (43.2).

Waldmann<sup>4</sup> has made numerical calculations and measurements for two cases. In the stationary case a tube with cross-section of the shape of a figure eight is considered. For part of the tube length the two halves of the "eight" are separated by a wall, and the two halves carry two different streaming gases. For the rest of the length, there is no separating wall, and the flowing gases diffuse into each other. Axial resistance thermometers measure the average temperature in each gas. If the average speed of the gas in both tubes is equal to  $\bar{W}$  (Equation [27.28]), we have

$$\int (T - T_0) dz = \frac{3}{64} d^2 \frac{\alpha}{\lambda} p \bar{W} (x_0' - x_0) \quad (52.2)$$

where  $d$  is the diameter of one half of the "eight," and  $x_0'$  and  $x_0$  are the original mole fractions of gas 1 in the two tubes;  $z$  is the coordinate along the axis, and the integral on the left side applies to either tube half, depending on which value of  $\alpha/\lambda$  is chosen. The experiments were made with a tube of 1 cm diameter and 50 cm length, for the pair  $N_2-H_2$ ;  $\alpha$  was found as 0.40 for  $x = 0.1$ , as 0.21 for  $x = 0.9$ .

For the nonstationary case, Waldmann developed the theory under the assumption that the gas is contained between two infinite plates a distance  $2L$  apart; at the beginning (temperature  $T_0$ ) there is a wall parallel to the plates midway between them, separating two gas mixtures of composition  $x_a$  and  $x_b$ . At a given moment, the partition is removed and the gases are allowed to diffuse. As for all diffusion problems, the general solution (as function of time, place and the constants) is rather complicated. For two cases, Waldmann gives values for the highest temperature difference  $T_a' - T_0$  in vessel  $a$ ,

<sup>2</sup> K. Clusius and L. Waldmann, *Naturwiss.*, **30**, 711 (1942); L. Waldmann, *Z. Physik*, **121**, 501 (1943); **123**, 28 (1944).

<sup>3</sup> C. C., p. 145, Equations (8.47), (8.37), (8.413); see also, S. R. de Groot, *J. de Physique*, **8**, 193 (1948).

<sup>4</sup> *Ibid.*, **124**, 175 (1948).

which is attained near the enclosing wall (for  $\alpha$  positive). If  $\lambda \gg D$ ,

$$T_a' - T_0 = \frac{D}{\lambda} \alpha T_0 \frac{R}{\alpha} \cdot \frac{(x_b - x_a)}{\alpha} \quad (52.3)$$

If  $\lambda = D$ , the factor  $D/\lambda$  is replaced by 0.24.

Independent of the value of  $D/\lambda$  we have for this geometry at a place with coordinate  $z$  (the origin is midway between the plates)

$$\int_0^\alpha (T - T_0) dt = -\alpha \frac{p}{\lambda} (x_b - x_a) z(z - L) \quad (52.4)$$

Experimentally the values of  $\alpha$  found in the mixture  $N_2-H_2$  with this method are, for  $x = 0.1$ ,  $\alpha = 0.42$ , for  $x = 0.9$ ,  $\alpha = 0.21$ , which agree very well with the values found in the stationary case and quoted above.

Waldmann <sup>5</sup> has also used a tube as diffusion vessel. This allows the determination of  $\alpha$ -values, provided it has once been standardized with a gas mixture of known  $\alpha$ . Waldmann proposes in general the use of the temperature changes, which are appreciable, as the much easier method for the determination of  $\alpha$  compared to the direct method.

L. Miller <sup>6</sup> has tested Waldmann's formulas for the nonstationary thermal diffusion effect for  $H_2-N_2$  mixtures and also has given results for other gas pairs. The interpretation is complicated by measurable effects of nonideality of the gas mixture even at normal pressure. Miller has also investigated the effect of diffusion from an open cylinder. Further development of these methods seems promising.

<sup>5</sup> L. Waldmann, *Z. Naturf.*, **2a**, 358 (1947).

<sup>6</sup> *Z. Naturforsch.*, **4a**, 262 (1949).





## CHAPTER II

# THE THERMODYNAMICS AND STATISTICAL MECHANICS OF REAL GASES

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The relations derived from the laws of perfect gases have the advantage of simplicity, which is sufficient justification for use of the expressions so obtained even under circumstances beyond their applicability. The laws themselves are strictly valid only in the limit of vanishing density, but some of the consequences of the laws are not true in this region. Even at atmospheric pressure the laws of perfect gases must be amended to attain high precision in the description of gaseous behavior, and, at the much higher pressures encountered in industrial syntheses and fractionation, the laws represent only the crudest sort of approximation and not even this in some respects. There is thus a clear, practical reason for studying the properties of real gases over a wide range of conditions. A second and equally cogent reason for such studies lies in their theoretical value. Our present knowledge of the nature and magnitude of intermolecular forces, which are a prime factor in almost all chemical phenomena, has been derived to a considerable extent from investigations of the gaseous state.

In this chapter the properties of gases *at equilibrium* are discussed. First the experimental pressure-volume-temperature relationships of pure and mixed real gases are described, and semi-empirical methods of correlation are treated.

Then a general thermodynamic theory of pure gases is presented, and three important methods for treating gas mixtures of variable composition, including mixtures in which chemical reaction may occur, are discussed. In this section the aim has been to state explicitly the assumptions on which the thermodynamic theory rests and not to include statistical methods at this stage of the argument.

There follows an application of the results to a variety of physicochemical problems. In view of the widespread usefulness of these relations, they have been given in considerable detail.

In the second part of the chapter the statistical mechanical theory of equilibrium states of real gases is presented. Attractive and repulsive forces and the complete intermolecular potential energy are discussed.

The theory of gases at moderate pressures and of the second virial coefficient is given for gases composed of various types of molecules; and the theory of gases at higher pressures and of the complete equation of state is developed. The statistical mechanical background for the theory of corresponding states and mixtures of real gases is also considered.

Any complete discussion of compressed gases would necessarily deal in considerable part with their non-equilibrium behavior, for example the phenomenon of mass, momentum, and heat transfer. These transport problems as well as the laws of reaction rate are the subjects of other chapters.

#### COMPRESSIBILITIES AND EQUATIONS OF STATE FOR GASEOUS SYSTEMS

(1) **Methods of Representation:** The relation among the pressure  $p$ , the molar volume  $v$  (the ratio  $V/n$  of the total volume  $V$  to the number of moles  $n$ ), and the absolute thermodynamic temperature  $T$  of a pure gas

$$f(p, v, T) = 0 \quad (1.1)$$

may be represented graphically or given by an equation. The latter is called the equation of state of the gas and contains a number of parameters known as the equation of state constants or simply the constants of the gas.

The quantities plotted in the graphical method depend on the problem to be solved. Frequently, use is made of the relation (1.1) for an ideal gas

$$pv = RT \quad (1.2)$$

where  $R$  is the universal gas constant. We may plot the deviation of some state property of a real gas from that given by Equation (1.2) as one of the coordinates or we may use Equation (1.2) as a guide to the choice of the quantities to be plotted.

With very few exceptions practical equations of state give the pressure as an explicit function of the molar volume and temperature:

$$p = \phi(v, T) \quad (1.3)$$

The equation explicit in the volume

$$v = \psi(p, T) \quad (1.4)$$

is less successful in representing the behavior of gaseous systems over the same range of temperature and pressure than the form explicit in the pressure when the same number of constants is used in each.

The expression corresponding to Equation (1.1) for a gas mixture composed of the constituents 1, 2,  $\dots$  at the mole numbers  $n_1, n_2, \dots$  is

$$F(p, v, T, x_1, x_2, \dots) = 0 \quad (1.5)$$

where  $v$  is the molar volume of the mixture,  $V/(\sum_i n_i)$ , and  $x_i$  is the mole fraction of the gas  $i$ ,  $n_i/(\sum_i n_i)$ .

Graphical methods for gas mixtures are not particularly useful except for mixtures of constant composition. When the composition is variable, the number of independent variables is too great for simple representation.

Theoretical and practical considerations indicate that for a gas mixture of constant composition relation (1.5) has the same form as (1.1), the equation of state constants of the pure gas being replaced by parameters that are functions

of the composition. The functions must contain the constants of the pure constituent gases in order that Equation (1.5) reduce to (1.1) for each  $x_i = 1$  but will include other constants arising from the interaction of unlike molecules. The interaction constants can be evaluated with sufficient accuracy for many purposes from the corresponding constants of the constituent gases by a method called "combination of constants." The term *equation of state of a gas mixture* denotes such an equation: one that permits computation of the pressure [volume] of a gas mixture from the volume [pressure], temperature, and mole numbers of the gases composing the mixture and the equation of state constants of the pure constituent gases. Thus the volumetric behavior of mixtures may be computed to a certain degree of approximation from data on the pure gases only.

For those regions in which an equation of state gives a sufficiently accurate representation of the compressibility, the analytic method would seem to be superior to the graphical method both for pure gases and mixtures of constant composition. The graphical method is hardly applicable to gas mixtures of variable composition.

(2) **Graphical Methods:** The computation of certain thermodynamic properties of pure gases is facilitated and the accuracy is increased by use of plots of the deviation functions:<sup>1</sup>

$$\alpha = v - \frac{RT}{p} \quad (2.1)$$

$$= v \left( \frac{pv}{RT} - 1 \right) \quad (2.2)$$

against the pressure or temperature.

Plots<sup>2</sup> of isothermals in the pressure-volume plane and of the compressibility factor  $Z$ ,

$$Z = \frac{pv}{RT} \quad (2.3)$$

against pressure or density at constant temperature have been used for certain purposes. Such plots for different gases have a similar general appearance but cannot be superimposed.

A graphical method that has found considerable use in engineering calculations especially when compressibility data for a gas are lacking but the critical pressure and temperature are known is based on the following considerations.

The discovery of the critical point between the liquid and gaseous states by Andrews<sup>3</sup> and the work of van der Waals<sup>4</sup> led to the law of corresponding

<sup>1</sup> G. N. Lewis and M. Randall, *Thermodynamics* (New York: McGraw-Hill Book Co., Inc., 1923), p. 195; W. E. Deming and L. E. Shupe, *Phys. Rev.*, **37**, 638 (1931).

<sup>2</sup> See, for instance, B. H. Sage, D. C. Webster, and W. N. Lacey, *Ind. Eng. Chem.*, **29**, 658 (1937).

<sup>3</sup> T. Andrews, *Phil. Trans. Roy. Soc. (London)*, **159**, 575 (1869).

<sup>4</sup> J. D. van der Waals, *Die Continuität des gasförmigen und flüssigen Zustandes*, Barth, Leipzig (1899–1900).

states according to which all gases have the same value of the reduced pressure  $p_r$  for the same reduced molar volume  $v_r$  and reduced temperature  $T_r$ . The reduced quantities are the dimensionless ratios

$$P_r = \frac{p}{p_c}, \quad v_r = \frac{v}{v_c}, \quad T_r = \frac{T}{T_c} \quad (2.4)$$

where the subscript  $c$  denotes the value of a quantity at the critical state. Thus a single surface in  $p_r$ - $v_r$ - $T_r$  space would represent the state behavior of all gases.

The law of corresponding states is only a rough approximation for real gases. It fell into disrepute but more recently has returned to favor in a somewhat

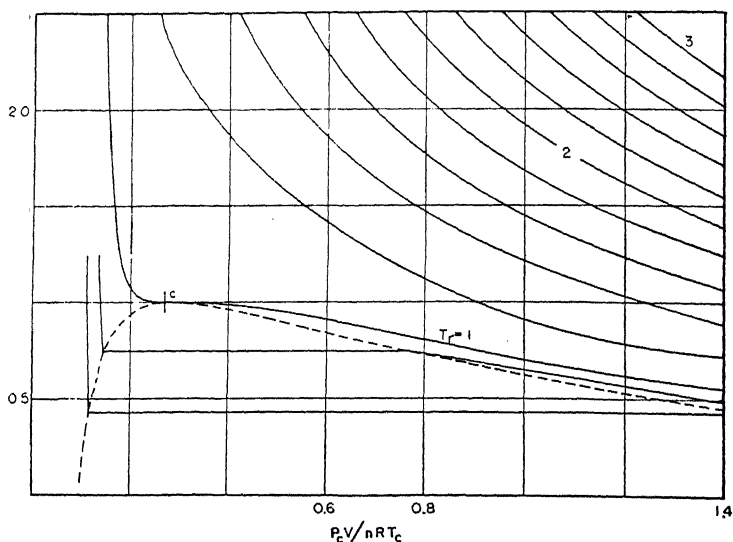


FIG. 1. Plot of the reduced pressure  $p_r$  against the pseudo-reduced volume  $(V/n)/(RT_c/p_c)$  for the reduced isotherms  $T_r$  from 1 to 3 in steps of 0.2. The critical point is marked  $c$ . The two-phase region is beneath the dotted curve. Two isotherms below the critical are sketched.

modified form.<sup>5</sup> One modification is based on the fact that the critical pressure and temperature of a substance are more readily determined and are known for more substances than the critical volume. Furthermore the critical ratio  $RT_c/p_c v_c$  is fairly constant for non-polar gases and has a value of about 3.42 for the monatomic and diatomic gases (except hydrogen and helium) and a value of about 3.65 when a large number of non-polar gases are included in the average. For these reasons the reduced volume  $v_r$  has been replaced by the

<sup>5</sup> J. Q. Cope, W. K. Lewis, and H. C. Weber, *Ind. Eng. Chem.*, **23**, 887 (1931); G. G. Brown, M. Souders, Jr., and R. L. Smith, *Ind. Eng. Chem.*, **24**, 513 (1932).

pseudo-reduced volume  $v_r'$

$$v_r' = RT_c/p_c - RT_c/p_c v_c \quad (2.5)$$

in certain graphical methods.

The contour lines of the reduced pressure-volume-temperature surface are drawn for several values of the reduced temperature  $T_r$  in Fig. 1.<sup>6</sup> The coordinates are the reduced pressure  $p_r$  and pseudo-reduced volume  $v_r'$ . If the law of corresponding states were exact, the plot would represent the behavior of all gaseous substances. Qualitatively the features to be noted are: (1) at

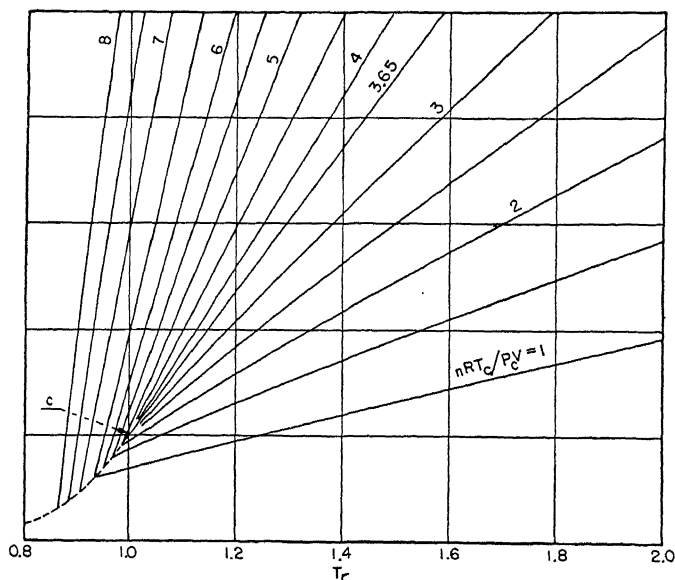


FIG. 2. Plot of the reduced pressure  $p_r$  against the reduced temperature  $T_r$  for the pseudo-reduced densities  $(RT_c/p_c)/(V/n)$  from 1 to 8 in steps of 0.5. The critical point is marked  $c$  and 3.65 is the critical pseudo-density. The vapor pressure curve is dotted.

high temperatures the isotherms approximate rectilinear hyperbolas except at small molar volumes, and at all temperatures the isotherms approach rectilinear hyperbolas at large molar volumes; (2) at lower temperatures (starting at about  $T_r = 1.1$ ) two inflection points become evident; (3) at one temperature, called the critical, the inflection point at the smaller molar volume has a horizontal tangent so that both the first and second derivatives of pressure with respect to volume are zero; (4) below the critical temperature each isotherm has a horizontal portion where the liquid and gas are in equilibrium, to the left of which the liquid curve rises steeply and to the right the gas curve starts concave

<sup>6</sup> This and the three following plots are taken from J. A. Beattie and W. H. Stockmayer, *Phys. Soc. (London), Reports on Progress in Physics*, 7, 195 (1940).

downward so that an inflection point must occur since at large molar volumes the curve is concave upward. The dotted curve separating the region of two phases from the regions of one phase is sometimes called the steam dome.

In Fig. 2 the reduced isometrics<sup>7</sup> showing the variation of  $p_r$  with  $T_r$  for a series of pseudo-reduced densities ( $1/v_r'$ ) are drawn. The isometrics have negative curvature (concave downward) from low reduced densities to about the critical where the curvature changes sign. At about twice the critical density the curvature becomes negative again.

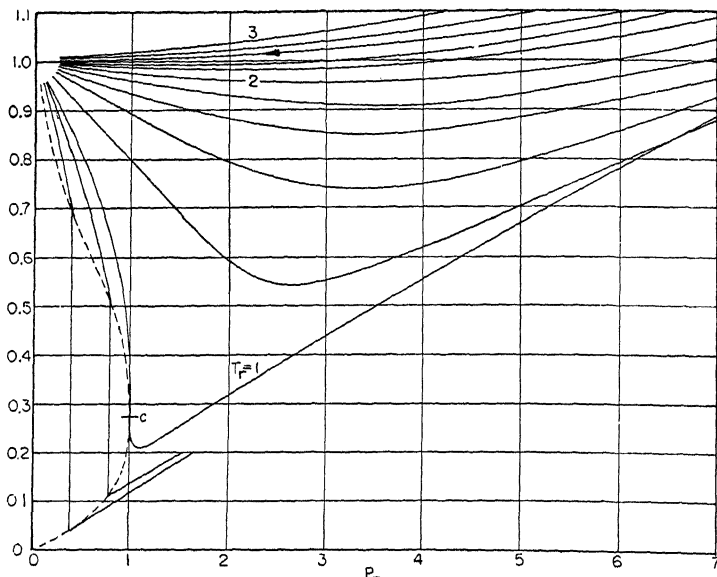


FIG. 3. Plot of the compressibility factor  $pV/nRT$  against the reduced pressure  $p_r$  for the reduced isotherms  $T_r$  from 1 to 3 in steps of 0.2. The critical point is marked  $c$  and the Boyle temperature (taken to be at  $T_r = 2.6$ ) denoted by an arrow. The two-phase region is to the left of the dotted curve. Two isotherms below the critical are sketched.

According to the law of corresponding states the compressibility factor depends only on the reduced state of a gas and is independent of the particular gas:

$$\frac{pv}{RT} = \left( \frac{p_r v_r}{RT_r} \right) \left( \frac{p_c v_c}{T_c} \right) \frac{p_r v_r'}{T_r} \quad (2.6)$$

In Fig. 3 is given a plot of  $Z$  against the reduced pressure  $p_r$  for several reduced temperatures  $T_r$ , and in Fig. 4 a plot of  $Z$  against the pseudo-reduced density ( $1/v_r'$ ) for several reduced temperatures. The isotherms of Fig. 3 below a temperature somewhat greater than the critical have a point of inflection, whereas the isotherms of Fig. 4 are always concave upward down to temperatures con-

<sup>7</sup> W. K. Lewis, *Ind. Eng. Chem.*, 28, 257 (1936).

siderably below the critical. When  $Z$  is plotted against the reduced pressure, the curves are vertical straight lines in the two-phase region; when plotted against the pseudo-reduced density, the curves are rectilinear hyperbolas in this region.

The foregoing four plots were made from an average of the properties of the lower hydrocarbons.<sup>8</sup> They represent the properties of these gases and the

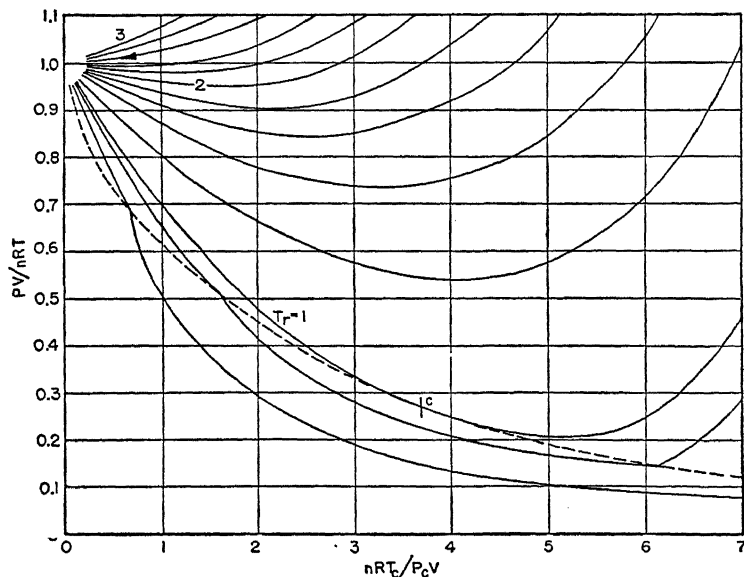


FIG. 4. Plot of the compressibility factor  $pV/nRT$  against the pseudo-reduced density  $(RT_c/p_c)/(V/n)$  for the reduced isotherms  $T_r$  from 1 to 3 in steps of 0.2. The critical point is marked  $c$  and the Boyle temperature denoted by an arrow. The two-phase region is beneath the dotted curve. Two isotherms below the critical are sketched.

non-polar gases except hydrogen and helium with an over-all accuracy of several per cent. Deviations for polar gases are larger. Hydrogen and helium are notable exceptions to the law of corresponding states; but the generalized reduced curves can be used for these gases, provided we use fictitious values<sup>8,9</sup> for the critical pressure and temperature rather than the true values.

The compressibility factor for a gas mixture of constant composition can be determined from Figs. 3 and 4. The true critical constants of the mixture are not used, but fictitious<sup>10</sup> ones are computed from the relations:

$$\begin{aligned} p_c(\text{mixture}) &= (\sum_i x_i p_{ci}) \\ T_c(\text{mixture}) &= (\sum_i x_i T_{ci}) \end{aligned} \quad (2.7)$$

<sup>8</sup> G.-J. Su and C.-H. Chang, *J. Am. Chem. Soc.*, **68**, 1080 (1946); G.-J. Su, *Ind. Eng. Chem.*, **38**, 803 (1946).

<sup>9</sup> R. H. Newton, *Ind. Eng. Chem.*, **27**, 302 (1935).

<sup>10</sup> W. B. Kay, *Ind. Eng. Chem.*, **28**, 1014 (1936).



where  $p_{ci}$  and  $T_{ci}$  are the critical constants of the constituent  $i$ , and  $x_i$  its mole fraction in the mixture.

(3) **Empirical Equations of State. Virial Coefficients:** Empirical equations of states expressing the pressure-volume product of a gas as an expansion in the density<sup>1</sup> or pressure<sup>2</sup> have been extensively used. These are usually written:

$$pv = A \left( 1 + \frac{B}{v} + \frac{C}{v^2} + \frac{D}{v^4} + \cdots \right) \quad (3.1)$$

$$pv = A + B'p + C'p^2 + D'p^4 + \cdots \quad (3.2)$$

where

$$A = A_0 \frac{T}{T_0} \quad (3.3)$$

and the coefficients  $B, C, \dots, B', C', \dots$  are functions of temperature. Theoretical considerations based on the virial theorem of Clausius would yield a relation similar to Equation (3.1) but containing all powers of  $1/v$ . As a practical matter of curve fitting, fewer terms are required if the odd powers of the density except the first are omitted.

It is evident that the function  $A$  must equal  $RT$ . But, in general, the investigators using these equations expressed density of gases in terms of the Amagat unit: the density of the gas at  $0^\circ\text{C}$  and 1 atm; or a similar unit: the density of the gas at  $0^\circ\text{C}$  and 1 meter of mercury. Thus the number of moles of gas in the system was not independently known.

The parameters  $B$  and  $C$  are called the second and third virial coefficients. Definite relations should exist between them and the corresponding parameters  $B'$  and  $C'$  of the infinite series (3.1) and (3.2):

$$B' = B \quad (3.4)$$

$$C' = \frac{C - B^2}{A}, \quad C = AC' + B'^2 \quad (3.5)$$

However if the two Equations (3.1) and (3.2) each with a finite number of terms are fitted to the same observations, the relations (3.4) and (3.5) hold only approximately, because of the failure of each equation written in closed form to give an exact representation of the data and of experimental errors in the data themselves. In general, for a given pressure range, Equation (3.1) fits the observations better than (3.2) when the same number of terms is used in each.

Figure 5 shows a plot of the second virial coefficient  $B$  against the reciprocal

<sup>1</sup> H. K. Onnes, *Leiden Comm. No. 71* (1901).

<sup>2</sup> L. Holborn, *Ann. Physik*, (4) **63**, 674 (1920); L. Holborn and J. Otto, *Z. Physik*, **33**, 1 (1925).

temperature for helium.<sup>3</sup> The coefficient is negative at low reduced temperatures, passes through zero somewhat above the critical temperature, rises to a maximum, and then decreases as the temperature is further increased. The second virial coefficients of other gases exhibit the same general trends, but the temperature of maximum  $B$  is above the region of compressibility measurements for all gases except hydrogen, helium, and neon.

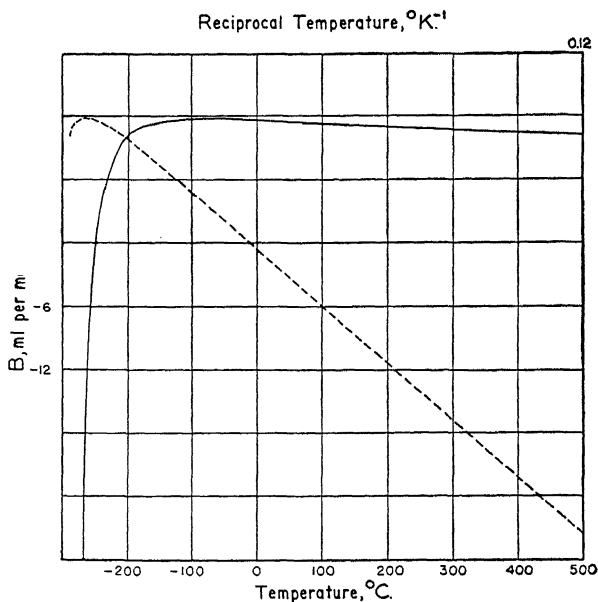


FIG. 5. Plot of the second virial coefficient  $B$  of helium against the Centigrade temperature (full line) and against the reciprocal Kelvin temperature (dotted line).

The temperature at which the second virial coefficient is zero is called the Boyle temperature.

Two other temperatures of importance are connected with the second virial coefficient. These are the inversion temperature of the Joule-Thomson effect at zero pressure and the inversion temperature of the Joule effect in the region of low pressures.

In the Joule-Thomson experiment a fluid flows through a porous plug in such a manner that its heat content  $H$  remains constant. The Joule-Thomson coefficient  $\mu_{J.T.}$  is defined as

$$\mu_{J.T.} = \left( \frac{\partial T}{\partial p} \right)_H \quad (3.6)$$

<sup>3</sup> For the values of  $B$  used, see F. G. Keyes, *Temperature* (New York: Reinhold Publishing Corporation, 1941), p. 45; W. G. Schneider and J. A. H. Duffie, *J. Chem. Phys.*, 17, 751 (1949).

whence from general thermodynamic relations we find:

$$\begin{aligned}\mu_{J.T.}C_p &= - \left( \frac{\partial H}{\partial p} \right)_T = T \left( \frac{\partial V}{\partial T} \right)_p - V \\ &= - \left[ \frac{\partial(V/T)}{\partial(1/T)} \right]_p = T^2 \left[ \frac{\partial(V/T)}{\partial T} \right]_p\end{aligned}\quad (3.7)$$

where  $C_p$  is the heat capacity at constant pressure. Evaluation of the last derivative from Equation (3.2) gives when we pass to the limit of zero pressure:

$$\lim_{p \rightarrow 0} \mu_{J.T.}C_p = - \frac{d(B/T)}{d(1/T)} = T^2 \frac{d(B/T)}{dT} \quad (3.8)$$

Since  $C_p$  remains finite, the zero-pressure Joule-Thomson coefficient passes through zero at the temperature at which  $B/T$  is a maximum. This is called the zero-pressure inversion temperature. Inversion temperatures at higher pressures evidently depend on the third and higher virial coefficients as well as on  $B$ . Equation (3.8) affords a means of computing <sup>4</sup> the change of the second virial coefficient with temperature from measurements of  $\mu_{J.T.}$  and  $C_p$  in the region of low pressures. The latter is usually computed from spectroscopic data. One value of  $B$  must be given, and this is taken from a well-studied isotherm, as  $0^\circ\text{C}$ .

In the Joule or free expansion experiment the energy  $E$  of a fluid remains constant. The Joule coefficient  $\eta$  is defined as

$$= - \left( \frac{\partial T}{\partial V} \right)_E \quad (3.9)$$

whence:

$$\eta C_V = \left( \frac{\partial E}{\partial V} \right)_T = T \left( \frac{\partial p}{\partial T} \right)_V - p = - \left[ \frac{\partial(p/T)}{\partial(1/T)} \right]_V = T^2 \left[ \frac{\partial(p/T)}{\partial T} \right]_V \quad (3.10)$$

where  $C_V$  is the heat capacity at constant volume. From Equation (3.1) we find for the region of low pressures:

$$\eta C_V = \frac{RT^2}{v^2} \frac{dB}{dT} + O \left( \frac{1}{v^3} \right) \quad (3.11)$$

where  $O(1/v^3)$  represents terms of the order of the cube of the density. As  $C_V$  remains finite, the Joule coefficient becomes zero at zero pressure. But at a density so small that terms of higher order may be neglected, the Joule coefficient has an inversion temperature at the maximum of the second virial coefficient. Above this temperature free expansion causes an increase rather than a decrease in the temperature of a gas. The experimental determination of Joule coefficients presents extraordinary difficulties and accurate values have never

<sup>4</sup> F. G. Keyes, *Temperature* (New York: Reinhold Publishing Corporation, 1941), p. 45.

been determined.<sup>5</sup> They may be computed <sup>6</sup> from other measurements through the relation:

$$\eta C_V = - \left[ \mu_{J.T.} C_p + \left( \frac{\partial(pV)}{\partial p} \right)_T \right] \left( \frac{\partial p}{\partial V} \right)_T \quad (3.12)$$

Keyes <sup>7</sup> finds the following values of the three characteristic temperatures for helium, hydrogen, and nitrogen from his correlation of all of the data available for determination of  $B$ . Some of the values are derived by extrapolation of the equations expressing  $B$  as a function of temperature and must be considered as estimates only.

Gas	Boyle Temperature $B = 0$	Low-Pressure Joule Inversion $B = \text{maximum}$	Zero-Pressure Joule-Thomson Inversion $\frac{B}{T} = \text{maximum}$
He	-249°C	- 77°C	-228°C
H <sub>2</sub>	-166	+ 443	- 72
N <sub>2</sub>	+ 51	+1867	+327

The third virial coefficient  $C$  is positive down to temperatures well below the critical; but the corresponding parameter  $C'$  though positive at higher temperatures passes through zero between the Boyle and critical temperatures.

From a kinetic viewpoint the second virial coefficient arises from binary encounters of molecules, and the third virial coefficient from ternary encounters. The general statistical theory of the  $k$ -th virial coefficient (the  $k$ -th term in the expansion of  $pv$  containing all powers of  $1/v$ ) has been worked out and is presented in a later paragraph.

When the molecular model is the rigid sphere of diameter  $\sigma$  with the attractive energy varying inversely as some power of the separation, say the theoretically correct inverse sixth power, we find for the second virial coefficient:

$$B = b - \frac{a}{RT} - O\left(\frac{1}{T^2}\right) \quad (3.13)$$

where  $O(1/T^2)$  represents terms of the order of  $1/T^2$  and

$$b = 2\pi N_0 \sigma^3 \quad a = N_0 b \epsilon \quad (3.14)$$

<sup>5</sup> See, for instance, F. G. Keyes and F. W. Sears, *Proc. Natl. Acad. Sci. U. S.*, **11**, 38 (1925).

<sup>6</sup> J. R. Roebuck and T. A. Murrell, *Temperature* (New York: Reinhold Publishing Corporation, 1941), p. 60.

<sup>7</sup> F. G. Keyes, *Temperature* (New York: Reinhold Publishing Corporation, 1941), p. 45.

In these relations  $N_0$  is the Avogadro number, and  $\epsilon$  the mutual potential energy of a pair of molecules in contact, that is, of separation  $\sigma$ . According to Equation (3.13),  $B$  increases with increasing temperature and has the limit  $b$  at infinite temperature. Thus the hard-sphere molecular model does not lead to a maximum in the second virial coefficient.

A special form of the potential introduced by Lennard-Jones,<sup>8</sup> based on a soft-sphere molecular model, represents the attractive potential energy of a pair of molecules by an inverse sixth power dependence on the separation, and the repulsive energy by an inverse twelfth power. The rather complicated expression for the second virial coefficient fits almost all data within experimental accuracy and predicts a maximum in  $B$ . The equation may be approximated very closely in the range  $\theta/T$  equal to 0.20 to 1.00 by the expression<sup>9</sup>

$$\frac{B}{\beta} = 0.71875 - 2.13189 \frac{\theta}{T} - 1.120795 \left( \frac{\theta}{T} \right)^2 \quad (3.15)$$

and in the same range to within the accuracy that  $B$  is known for most gases by the simpler relation

$$\frac{B}{\beta} = \left( \frac{\theta}{T} \right)^{1/4} \left( 1.064 - 3.602 \frac{\theta}{T} \right) \quad (3.16)$$

Here:

$$\beta = \frac{2\pi N_0 \sigma^3}{3} \quad (3.17)$$

$$\theta = \frac{\epsilon}{k}$$

where  $\sigma$  is the separation of a pair of molecules for zero potential energy,  $\epsilon$  the magnitude of the potential energy minimum, and  $k$  Boltzmann's constant.

The third virial coefficient for the Lennard-Jones (6, 12) potential has been evaluated numerically by two groups of investigators<sup>10, 11</sup> with somewhat discordant results. These integrations are considered in a later paragraph.

(4) **Early Semi-Empirical Equations of State:** A great number of equations of state with a more or less rational basis has been proposed. In order to be useful an equation of state must be of such a form that evaluation of the constants from experimental data can be readily accomplished and mathematical manipulation easily executed.

<sup>8</sup> J. E. Lennard-Jones, *Proc. Roy. Soc. (London)*, **A106**, 463 (1924).

<sup>9</sup> W. H. Stockmayer and J. A. Beattie, *J. Chem. Phys.*, **7**, 476 (1942).

<sup>10</sup> J. de Boer and A. Michels, *Physica*, **6**, 97 (1939).

<sup>11</sup> J. E. Mayer and E. Montroll, *J. Chem. Phys.*, **9**, 626 (1941).

Three classical equations of state have received considerable attention:

$$p = \frac{nRT}{V - nb} - \frac{n^2a}{V^2} \quad (\text{van der Waals } ^1) \quad (4.1)$$

$$p = \frac{nRT}{V - nb} \cdot e^{-na/VRT} \quad (\text{Dieterici } ^2) \quad (4.2)$$

$$p = \frac{nRT}{V - nb} - \frac{n^2a}{TV^2} \quad (\text{Berthelot } ^3) \quad (4.3)$$

None of these equations gives a good representation of the compressibility of gases over a wide range of pressure and temperature, yet the leading features of the pressure-volume-temperature surface are qualitatively represented; and the equations, especially that of van der Waals, have inspired much theoretical and experimental work.

All of the equations give isothermals similar to those plotted in Fig. 1, with one pressure-volume curve having a horizontal inflection point at which there are three real coincident values of  $v$ . Below this temperature the equations give continuous isothermal curves with continuous first derivatives. In the region of equilibrium between liquid and vapor phases the isothermals have a maximum and a minimum similar to the continuous isotherm postulated by Thomson <sup>4</sup> on the basis of a study of Andrews' data on the compressibility of carbon dioxide. Thus all three equations of state provide for a liquid-gas critical point.

In regard to pressure-temperature curves at constant molar volume, van der Waals' equation requires linear isometrics; Dieterici's, isometrics of positive curvature; and Berthelot's, isometric with negative curvature. Berthelot was primarily interested in a low pressure equation of state for the permanent gases to be used in the correction of gas thermometric measurements for the imperfection of the gas. His equation gives the correct sign of the curvature of the isometrics in this region.

The equations of van der Waals and Dieterici give for the second virial coefficient

$$B = b - \frac{a}{RT} \quad (4.4)$$

while that of Berthelot gives

$$B = b - \frac{a}{RT^2}. \quad (4.5)$$

All predict a Boyle temperature, but none requires a maximum in  $B$ . The

<sup>1</sup> J. D. van der Waals, *Die Continuität des gasförmigen und flüssigen Zustandes*, Barth, Leipzig (1899-1900).

<sup>2</sup> C. Dieterici, *Ann. Physik*, **69**, 685 (1899).

<sup>3</sup> D. Berthelot, *Trav. Bur. Int. Poids Mes.*, **13**, 113 pp. (1907).

<sup>4</sup> J. Thomson, *Proc. Roy. Soc. (London)*, **20**, 1 (1871).

relation (4.4) is the first two terms of (3.13), which was derived for a hard-sphere molecular model.

Three conditions hold at the critical point of a substance: the equation of state  $f(p, v, T) = 0$ , the condition of a horizontal tangent to the critical isotherm  $(\partial p / \partial v)_T = 0$ , and the condition of a point of inflection  $(\partial^2 p / \partial v^2)_T = 0$ . These are sufficient to permit evaluation of the three critical constants in terms of  $R$ ,  $a$ , and  $b$ ; or conversely to express  $R$ ,  $a$ , and  $b$  in terms of  $p_c$ ,  $v_c$ , and  $T_c$ . When the resulting values of  $R$  and the two equation of state constants are substituted into the original equation of state, there results a relation among the reduced pressure, reduced volume, and reduced temperature that contains no constants characteristic of the gas. Written in terms of the pressure, volume, and temperature the equation of state contains the three critical constants as parameters.

In Table I is given under the heading of "van der Waals' Equation," "Dieterici's Equation," and "Berthelot's Equation" a group of relations peculiar to each: the first line gives the equation of state written for one mole of gas; the second gives the virial form of each equation to terms of the order of  $p^2$ , the coefficient of  $p$  being the second virial coefficient  $B$  as defined by Equation (3.1) or (3.2); the third and fourth lines give the values of  $R$ ,  $a$ , and  $b$  in terms of  $p_c$ ,  $v_c$ , and  $T_c$ , and the converse relations; the fifth and sixth lines give the reduced equations of state corresponding to the forms written in the first and second lines; and the last line gives the virial equation of state in terms of  $p$ ,  $v$ , and  $T$  but with the second virial coefficient (the expression in brackets) stated in terms of the critical pressure and temperature and the reduced temperature. This relation may be compared with that in the second line.

TABLE I  
REDUCED FORMS OF EQUATIONS OF STATE  
van der Waals' Equation

$$\begin{aligned}
 p &= \frac{RT}{v-b} - \frac{a}{v^2} \\
 pv &= RT + \left(b - \frac{a}{RT}\right)p + O(p^2) \\
 p_c &= \frac{8a}{27b^2} \quad v_c = 3b \quad T_c = \frac{8a}{27Rb} \\
 b = \frac{v_c}{3} = \frac{1}{8} \frac{RT_c}{p_c} \quad a = 3p_c v_c^2 = \frac{27}{64} \frac{R^2 T_c^2}{p_c} \quad R = \frac{8}{3} \frac{p_c v_c}{T_c} \quad \frac{RT_c}{p_c v_c} = \frac{8}{3} = 2.67 \\
 p_r &= \frac{8T_r}{3v_r - 1} - \frac{3}{v_r^2} \\
 p_r v_r &= \frac{8}{3} T_r + \left(\frac{1}{3} - \frac{9}{8T_r}\right)p_r + O(p_r^2) \\
 pv &= RT + \left\{ \frac{RT_c}{p_c} \left( \frac{1}{8} - \frac{27}{64T_r} \right) \right\} p + O(p^2)
 \end{aligned}$$

TABLE I—Continued

Dieterici's Equation

$$p = \frac{RT}{v - b} e^{-a/vRT}$$

$$pv = RT + \left(b - \frac{a}{RT}\right) p + O(p^2)$$

$$p_c = \frac{a}{4e^2b^2} \quad v_c = 2b \quad T_c = \frac{a}{4Rb}$$

$$b = \frac{v_c}{2} = \frac{1}{e^2} \frac{RT_c}{p_c} \quad a = e^2 p_c v_c^2 = \frac{4}{e^2} \frac{R^2 T_c^2}{p_c} \quad R = \frac{e^2 p_c v_c}{2 T_c} \quad \frac{RT_c}{p_c v_c} = \frac{e^2}{2} = 3.69$$

$$p_r = \frac{T_r}{2v_r - 1} e^{2-2/T_r v_r}$$

$$p_r v_r = \frac{e^2}{2} T_r + \left(\frac{1}{2} - \frac{2}{T_r}\right) p_r + O(p_r^2)$$

$$pv = RT + \left\{ \frac{RT_c}{p_c} \left( \frac{1}{e^2} - \frac{4}{e^2 T_r} \right) \right\} p + O(p^2)$$

Berthelot's Equation

$$p = \frac{RT}{v - b} - \frac{a}{T v^2}$$

$$pv = RT + \left(b - \frac{a}{RT^2}\right) p + O(p^2)$$

$$p_c^2 = \frac{aR}{216b^3} \quad v_c = 3b \quad T_c^2 = \frac{8a}{27Rb}$$

$$b = \frac{v_c}{3} = \frac{1}{8} \frac{RT_c}{p_c} \quad a = 3p_c v_c^2 T_c = \frac{27}{64} \frac{R^2 T_c^3}{p_c} \quad R = \frac{8}{3} \frac{p_c v_c}{T_c} \quad \frac{RT_c}{p_c v_c} = \frac{8}{3} = 2.67$$

$$p_r = \frac{8T_r}{3v_r - 1} - \frac{3}{T_r v_r^2}$$

$$p_r v_r = \frac{8}{3} T_r + \left(\frac{1}{3} - \frac{9}{8T_r^2}\right) p_r + O(p_r^2)$$

$$pv = RT + \left\{ \frac{RT_c}{p_c} \left( \frac{1}{8} - \frac{27}{64T_r^2} \right) \right\} p + O(p^2)$$

Berthelot's Equation with Empirical Value of Critical Ratio

$$b = \frac{v_c}{4} = \frac{9}{128} \frac{RT_c}{p_c} \quad a = \frac{16}{3} p_c v_c^2 T_c = \frac{27}{64} \frac{R^2 T_c^3}{p_c} \quad R = \frac{32}{9} \frac{p_c v_c}{T_c} \quad \frac{RT_c}{p_c v_c} = \frac{32}{9} = 3.56$$

$$p_r = \frac{128}{9} \frac{T_r}{4v_r - 1} - \frac{16}{3T_r v_r^2}$$

$$p_r v_r = \frac{32}{9} T_r + \left(\frac{1}{4} - \frac{3}{2T_r^2}\right) p_r + O(p_r^2)$$

$$pv = RT + \left\{ \frac{RT_c}{p_c} \left( \frac{9}{128} - \frac{27}{64T_r^2} \right) \right\} p + O(p^2)$$



Dieterici's equation gives a critical ratio 3.69 close to the average 3.65 for a large number of non-polar gases, the other two give critical ratios far below this average. Berthelot proposed an empirical set of values of  $R$ ,  $a$ , and  $b$  in terms of critical constants, not consistent with his equation of state, but yielding a critical ratio of 3.56 closer to the average value 3.4 for the simpler gases. Substitution of these empirical values into his equation yields the relation given in the second line of the last section of Table I. The last two lines are approximations of this to terms of the order of  $p^2$ . The last equation has been used frequently for correction of thermodynamic results for gas imperfection in the region of low pressure. Only the critical pressure and temperature need be known.

It was a cardinal point of the earlier workers that the equation of state constants be determined from critical data alone and not from the actual compressibility of a gas. As a result the compilations of van der Waals' constants found in various handbooks are utterly worthless for computing the volumetric behavior of gases.

(5) **Later Semi-Empirical Equations of State:** The following equations of state are more successful in representing the compressibility of gases:

$$p = \frac{nRT}{V - n\delta} - \frac{n^2A}{(V + nl)^2} \quad \delta = \beta e^{-na/V} \quad (\text{Keyes}^1) \quad (5.1)$$

$$\begin{aligned} \frac{nRT(1 - \epsilon)}{V^2} [V + nB] - \frac{n^2A}{V^2} &= B_0 \left(1 - \frac{nb}{V}\right) \\ &(\text{Beattie-Bridgeman}^2) \\ &= A_0 \left(1 - \frac{na}{V}\right) \\ \epsilon &= \frac{nc}{VT^3} \end{aligned} \quad (5.2)$$

or:

$$\begin{aligned} p &= T\psi(d) - \phi(d) - \frac{\Gamma(d)}{T^2} \quad \psi(d) = Rd(1 + B_0d - B_0bd^2) \\ &\quad \phi(d) = A_0d^2 - A_0ad^3 \\ &\quad \Gamma(d) = Rcd^2(1 + B_0d - B_0bd^2) \\ &\quad d \equiv \frac{n}{V} \end{aligned} \quad (5.2)$$

$$\begin{aligned} p &= T\psi(d) - \phi(d) - \frac{\Gamma(d)}{T^2} \quad \psi(d) = Rd(1 + B_0d + bd^2) \\ &\quad (\text{Benedict-Webb-Rubin}^3) \\ &\quad \phi(d) = A_0d^2 + ad^3 - \alpha\alpha d^6 \\ &\quad \Gamma(d) = C_0d^2 - cd^3(1 + \gamma d^2) \exp(-\gamma d^2) \end{aligned} \quad (5.3)$$

<sup>1</sup> F. G. Keyes, *J. Amer. Soc. Refrig. Engrs.*, 1, 9 (1914); *Proc. Natl. Acad. Sci. U. S.*, 3, 323 (1917).

<sup>2</sup> J. A. Beattie and O. C. Bridgeman, *J. Am. Chem. Soc.*, 49, 1665 (1927); *Proc. Amer. Acad. Arts Sci.*, 63, 229 (1928).

<sup>3</sup> M. Benedict, G. B. Webb, and L. C. Rubin, *J. Chem. Phys.*, 8, 344 (1940).

These equations have four, five, and eight adjustable constants, respectively. The representation of gas compressibility is increasingly better as the number of constants increase. Equation (5.2) is fairly satisfactory to the critical density for temperatures above the critical; Equation (5.3) to about twice the critical density and down to temperatures well below the critical.

Each of the equations predicts a critical isotherm with a horizontal inflection point. Below this temperature the isotherms are of the type postulated by Thomson, the liquid and vapor isotherms of the same temperature being connected by a smooth curve with a maximum and a minimum in the two-phase region. Since the free energies of a pure liquid and its vapor in isothermal equilibrium are equal, the two areas in the two-phase region enclosed between the continuous isotherm and the vapor pressure line must be equal. Application of this principle to the Benedict-Webb-Rubin equation permits calculation of vapor pressures and saturated liquid and vapor volumes with satisfactory accuracy. The actual method of calculation consists in computing both the pressure (from the equation of the state) and the fugacity (from the integration of the general thermodynamic relation for fugacity by means of the equation of state) for a series of molar volumes at a constant temperature in the vapor and in the liquid region. The fugacity is plotted against the pressure for each phase. The intersection of the curves gives the vapor pressure, from which the saturated liquid and vapor volumes can be determined.

Equation (5.1) requires linear isometrics, (5.2) isometrics with negative curvature throughout the entire density range, while (5.3) permits negative curvature at low densities, positive at intermediate densities, and negative again at high densities in agreement with the observed behavior of gases. The sign of the curvature is determined by the sign of  $\Gamma(d)$ :

$$\left( \frac{\partial^2 p}{\partial T^2} \right)_v = - \frac{6\Gamma(d)}{T^4} \quad (5.4)$$

The Keyes equation of state gives for the second virial coefficient

$$B = \beta - \frac{A}{RT} \quad (5.5)$$

while the other two give a relation of the type

$$B = B_0 - \frac{A_0}{RT} - \frac{c}{T^3} \quad (5.6)$$

where  $c$  is replaced by  $C_0$  in the Benedict-Webb-Rubin equation. Thus all three equations of state are based on a hard-sphere molecular model. They do not provide for a maximum in the second virial coefficient. This deficiency is not serious from the standpoint of representing compressibility data except for helium and possibly hydrogen and neon.

All three equations of state have too many constants to be determined uniquely in terms of the three critical constants of a gas, and reduced equations

of the type of those discussed in the last section cannot be derived. One method of introducing the critical constants and writing a reduced equation of state is given in a later section.

For polar gases Keyes <sup>4</sup> writes

$$p = \frac{RT}{v - B'} \quad B' = B + f(p, T) \quad (5.7)$$

$$B = B_0 - \frac{A}{RT} e^{D/T}$$

where  $f(p, T)$  contains six constants for water vapor. This gives for the second virial coefficient  $B$

$$B = B_0 - \frac{A}{RT} e^{D/T^2} \quad (5.8)$$

For non-polar gases at not too low temperatures  $D/T^2$  is small, and the exponential may be expanded to give

$$B = B_0 - \frac{A}{RT} - \frac{AD}{RT^3} - \dots \quad (5.9)$$

in agreement with Equation (5.6) to the first three terms.

(6) **The Beattie-Bridgeman Equation of State:** The equation of state (5.2) can be written in the virial form

$$\frac{pV}{n} = RT + \frac{n\beta}{V} + \frac{n^2\gamma}{V^2} + \frac{n^3\delta}{V^3} \quad (6.1)$$

$$\beta = RTB_0 - A_0 - \frac{Rc}{T^2}$$

$$\gamma = -RTB_0b + A_0a - \frac{RB_0c}{T^2}$$

$$\delta = \frac{RB_0bc}{T^2}$$

Pressure and temperature are the usual independent variables employed for reporting experimental results. For the integration of the equations stating the thermodynamic properties of gases in terms of these independent variables, we desire an equation of state expressing the density as a function of pressure and temperature. Such an equation of manageable form and with a relatively few parameters does not exist. We may make several approximations to Equation (6.1) that give reasonably good representation of the density over certain restricted ranges.

In the first and most exact approximation <sup>1</sup> Equation (6.1) is expanded in

<sup>4</sup> F. G. Keyes, L. B. Smith, and H. T. Gerry, *Proc. Amer. Acad. Arts Sci.*, **70**, 319 (1936);

F. G. Keyes, *J. Am. Chem. Soc.*, **60**, 1761 (1938); *J. Chem. Phys.*, **17**, 923 (1949).

<sup>1</sup> G. Scatchard, *Proc. Natl. Acad. Sci., U. S.*, **16**, 811 (1930).

terms of itself:

$$\frac{V}{n} = \frac{RT}{p} + \frac{\beta}{RT} + \left[ \frac{\gamma}{(RT)^2} - \frac{\delta}{(RT)^3} \right] p + \left[ \frac{\delta}{(RT)^3} - \frac{3\beta\gamma}{(RT)^4} + \frac{2\beta^2}{(RT)^5} \right] p^2 \quad (6.2)$$

This equation gives  $pV/n$  to terms of the order of  $p^3$ . A less exact form would be obtained by replacing  $n/V$  by  $p/RT$  in each term on the right-hand side of Equation (6.1):

$$\frac{V}{n} = \frac{RT}{p} + \frac{\beta}{RT} + \frac{\gamma}{(RT)^2} p + \frac{\delta}{(RT)^3} p^2 \quad (6.3)$$

The equation<sup>2</sup> would probably give a better representation of the density of gases than Equation (6.2), provided we redetermined the values of the parameters  $A_0$ ,  $a$ ,  $B_0$ ,  $b$  and  $c$  for this form of equation. To do this we would need to resmooth all of the compressibility data to give densities at each temperature for an evenly spaced set of values of  $p/RT$ . Then in place of Equation (5.2) we would write

$$\begin{aligned} \frac{V}{n} &= \left( \frac{RT}{p} + B \right) (1 - \epsilon) - \frac{A}{RT} & A &= A_0 \left( 1 - \frac{ap}{RT} \right) \\ B &= B_0 \left( 1 - \frac{bp}{RT} \right) & B &= B_0 \left( 1 - \frac{bp}{RT} \right) \\ \epsilon &= \frac{c}{T^3} \frac{p}{RT} & \epsilon &= \frac{c}{T^3} \frac{p}{RT} \end{aligned} \quad (6.4)$$

Thus we would have two sets of the equation of state parameters: one for Equation (5.2) or (6.1) and one for Equation (6.3) or (6.4). Unfortunately the values of the parameters for Equation (6.3) have not yet been determined and we are forced to use those determined for Equation (6.1).

Sufficient accuracy is obtained in many thermodynamic calculations if we drop the last two terms of Equation (6.3) and write

$$\frac{V}{n} = \frac{RT}{p} + \frac{\beta}{RT} \quad (6.5)$$

using the values of the parameters  $A_0$ ,  $B_0$ , and  $c$  determined for use in Equation (6.1). This very approximate equation is entirely inadequate for computation of the density of a gas but gives excellent results in the calculation of the effect of pressure on the mass action constant, doubtless through a compensation of errors.

The constants of the equation explicit in the pressure are given for several gases in Table II. When the constants are not known, they may be approximated by the method given in the next paragraph.

<sup>2</sup> J. A. Beattie, *Proc. Natl. Acad. Sci., U. S.*, 16, 14 (1930).

TABLE II

VALUES OF THE CONSTANTS OF THE BEATTIE-BRIDGEMAN EQUATION  
OF STATE FOR SEVERAL GASES

$$p = [RT(1 - \epsilon)/V^2][V + B] - A/V^2$$

$$A = A_0(1 - a/V) \quad B = B_0(1 - b/V) \quad \epsilon = c/VT^3$$

Units: normal atmospheres; liters per mole; °K ( $T^\circ\text{K} = t^\circ\text{C} + 273.13$ );  $R = 0.08206$

Gas	$A_0$	$B_0$	$10^{-4} \times c$	Molecular Weight
He.....	0.0216	0.05984	0.01400	4.00
Ne.....	0.2125	0.02196	0.02060	20.2
A.....	1.2907	0.02328	0.03931	39.91
H <sub>2</sub> .....	0.1975	-0.00506	0.02096	2.0154
N <sub>2</sub> .....	1.3445	+0.02617	0.05046	28.016
O <sub>2</sub> .....	1.4911	0.02562	0.04624	32
Air.....	1.3012	0.01931	0.04611	28.964
I <sub>2</sub> .....	17.0	0.325	4000	253.864
CO <sub>2</sub> .....	5.0065	0.07132	0.10476	44.000
NH <sub>3</sub> .....	2.3930	0.17031	0.03415	17.0311
CH <sub>4</sub> .....	2.2769	0.01855	0.05587	16.0308
C <sub>2</sub> H <sub>4</sub> .....	6.1520	0.04964	0.12156	28.0308
C <sub>2</sub> H <sub>6</sub> .....	5.8800	0.05861	0.09400	30.0462
C <sub>3</sub> H <sub>8</sub> .....	11.9200	0.07321	0.18100	44.0616
1-C <sub>4</sub> H <sub>8</sub> .....	16.6979	0.11988	0.24046	56.0616
iso-C <sub>4</sub> H <sub>8</sub> .....	16.9600	0.10860	0.24200	56.0616
n-C <sub>4</sub> H <sub>10</sub> .....	17.7940	0.12161	0.24620	58.077
iso-C <sub>4</sub> H <sub>10</sub> .....	16.6037	0.11171	0.23540	58.077
n-C <sub>5</sub> H <sub>12</sub> .....	28.2600	0.15099	0.39400	72.0924
neo-C <sub>5</sub> H <sub>12</sub> .....	23.3300	0.15174	0.33560	72.0924
n-C <sub>7</sub> H <sub>16</sub> .....	54.520	0.20066	0.70816	100.1232
CH <sub>3</sub> OH.....	33.309	0.09246	0.60362	32.0308
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O.....	31.278	0.12426	0.45446	74.077

Gas	$A_0^{1/2}$	$B_0^{1/3}$	$10^{-2} \times c^{1/2}$	Gas	$A_0^{1/2}$	$B_0^{1/3}$	$10^{-2} \times c^{1/2}$
He..	0.14697	0.241014	0.0632	C <sub>2</sub> H <sub>4</sub> .....	2.48032	0.495371	4.7624
Ne..	0.46098	0.274129	0.3178	C <sub>2</sub> H <sub>6</sub> .....	2.42487	0.454684	9.4868
A....	1.13609	0.340017	2.4474	C <sub>3</sub> H <sub>8</sub> .....	3.45254	0.565665	10.9545
H <sub>2</sub> ...	0.44441	0.275717	0.2245	1-C <sub>4</sub> H <sub>8</sub> ....	4.08631	0.621843	17.3205
N <sub>2</sub> ...	1.15953	0.369529	2.0494	iso-C <sub>4</sub> H <sub>8</sub> ...	4.11825	0.623168	15.8114
O <sub>2</sub> ...	1.22111	0.358927	2.1909	n-C <sub>4</sub> H <sub>10</sub> ...	4.21829	0.626752	18.7083
Air..	1.14070	0.358590	2.0833	iso-C <sub>4</sub> H <sub>10</sub> ...	4.07476	0.617451	17.3205
I <sub>2</sub> ...	4.12311	0.687534	63.2456	n-C <sub>5</sub> H <sub>12</sub> ...	5.31601	0.733104	20.0000
CO <sub>2</sub> ..	2.23752	0.471410	8.1240	neo-C <sub>5</sub> H <sub>12</sub> ...	4.83011	0.694929	20.0000
NH <sub>3</sub> ..	1.54693	0.324437	21.8374	n-C <sub>7</sub> H <sub>16</sub> ...	7.38377	0.891341	20.0000
CH <sub>4</sub> ..	1.50894	0.382290	3.5819	CH <sub>3</sub> OH....	5.77139	0.845126	5.6595
				(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O...	5.59267	0.768833	5.7732

(7) **Approximate Reduced Equation of State. Computation of the Constants from Critical Data.** Other Relations Among the Constants: The equation of state (5.2) or (6.1) contains too many constants—six including the gas constant  $R$ —to be expressed uniquely in terms of the three critical constants of a gas through the three conditions at the critical point. We may, however, proceed as follows. In Equation (6.1) each molar volume  $v$  can be written in terms of the pseudo-reduced volume defined in Equation (2.5):

$$RT_c \quad (7.1)$$

Then Equation (6.1) becomes<sup>1</sup>

$$\begin{aligned} p_r v_r' &= T_r + \frac{\beta_r}{v_r'} + \frac{\gamma_r}{v_r'^2} + \frac{\delta_r}{v_r'^3} \\ \beta_r &= \frac{p_c}{(RT_c)} \quad T_r B_{0r} - A_{0r} - \frac{\gamma_r}{T_r^2} \\ \gamma_r &= \frac{p_c^2}{(RT_c)^3} \gamma = -T_r B_{0r} b_r + A_{0r} a_r - \frac{B_{0r} c_r}{T_r^2} \\ \delta_r &= \frac{p_c^3}{(RT_c)^4} \delta = \frac{B_{0r} b_r c_r}{T_r^2} \end{aligned} \quad (7.2)$$

The dimensionless ratios  $\beta_r$ ,  $\gamma_r$ ,  $\delta_r$  may be considered the reduced virial parameters; and the dimensionless ratios

$$\begin{aligned} A_{0r} &= \frac{A_{0r}}{RT_c^2/p_c}, & B_{0r} &= \frac{B_{0r}}{RT_c/p_c}, & RT_c^4/p_c \\ a_r &= \frac{a_r}{RT_c/p_c}, & b_r &= \frac{b_r}{RT_c/p_c} \end{aligned} \quad (7.3)$$

may be considered the reduced equation of state constants of a gas.

The ratios  $A_{0r}$ ,  $B_{0r}$ , and  $c_r$  were found by Keyes<sup>2</sup> to be fairly constant for a number of non-polar gases. We might employ the relations (7.3) in any one of a number of ways in order to obtain the equation of state constants for use in Equation (6.1) when compressibility data on a gas are lacking but its critical pressure and temperature are known: (1) Compute<sup>3</sup> values of the reduced constants from some one gas, say nitrogen, and then use these to compute the equation of state constants for the gas whose compressibility has not been measured; (2) use the same procedure but use as a reference gas one whose structure is similar to the gas of unknown constants; (3) resmooth the compressibility data on a number of gases to give reduced pressures in terms of

<sup>1</sup> G.-J. Su and C.-H. Chang, *J. Am. Chem. Soc.*, **68**, 1080 (1946).

<sup>2</sup> F. G. Keyes, *J. Am. Chem. Soc.*, **60**, 1761 (1938).

<sup>3</sup> S. H. Maron and D. Turnbull, *Ind. Eng. Chem.*, **33**, 408 (1941); F. W. Brown, *Ind. Eng. Chem.*, **33**, 1536 (1941).

reduced temperatures for a series of pseudo-reduced isometrics, average the resulting reduced pressures, and determine a single set of reduced equation of state constants. The latter has been done <sup>4</sup> from the compressibility data on seven hydrocarbons, and the reduced constants so obtained were used to calculate the pressures of nine other gases, not hydrocarbons, over a range of density and temperature with satisfactory results. The values of the reduced constants determined in this way are

$$\begin{aligned} A_{or} &= 0.4758 & a_r &= 0.1127 \\ B_{or} &= 0.18764 & b_r &= 0.03833 \\ c_r &= 0.05 \end{aligned} \quad (7.4)$$

Thus for the equation of state constants of a gas expressed in terms of its critical pressure and temperature we find

$$\begin{aligned} A_0 &= 0.4758 \left( \frac{RT_c}{p_c} \right)^2 p_c & a &= 0.1127 \left( \frac{RT_c}{p_c} \right) \\ B_0 &= 0.18764 \left( \frac{RT_c}{p_c} \right) & b &= 0.03833 \left( \frac{RT_c}{p_c} \right) \\ c &= 0.05 \left( \frac{RT_c}{p_c} \right) T_c^3 \end{aligned} \quad (7.5)$$

The approximate Equation (6.5) can be written

$$\begin{aligned} pv &= RT + \frac{RT_c}{p_c} \left( B_{or} - \frac{A_{or}}{T_r} - \frac{c_r}{T_r^3} \right) p \\ &= RT + \frac{RT_c}{p_c} \left( 0.18764 - \frac{0.4758}{T_r} - \frac{0.05}{T_r^3} \right) p \end{aligned} \quad (7.6)$$

This equation is preferable to Berthelot's equation given in Table I for the approximate correction of low pressure thermodynamic data for the imperfection of the gas.

From a corresponding states study of the equation of state constants as determined from experimental data Keyes <sup>5</sup> found empirically

$$c = 0.023 \frac{A_0^3}{R^3 B_0^2} \quad (7.7)$$

for non-polar gases. Hirschfelder and Roseveare <sup>6</sup> found 0.024 for the coefficient on theoretical grounds by use of a (6, 12) Lennard-Jones potential, and Corner <sup>7</sup> found 0.013 when a (6, 9) potential was used. Corner also extended the method to the third virial coefficient and gave the theoretical relations

$$a = 0.45B_0, \quad b = 0.1B_0 \quad (7.8)$$

<sup>4</sup> G.-J. Su and C.-H. Chang, *loc. cit.*

<sup>5</sup> F. G. Keyes, *J. Am. Chem. Soc.*, **60**, 1761 (1938).

<sup>6</sup> J. O. Hirschfelder and W. E. Roseveare, *J. Phys. Chem.*, **43**, 15 (1939).

<sup>7</sup> J. Corner, *Trans. Faraday Soc.*, **37**, 358 (1941).

The constants of many of the non-polar gases are in fair agreement with these relations.

(8) **Dalton's Law and Amagat's Law for Gas Mixtures:** The usual statement of Dalton's law <sup>1</sup> is: The pressure of a mixture of gases is equal to the sum of the pressures of the different gases as existing each by itself at the same temperature and in a volume equal to the total volume of the mixture. This may be called the law of the additivity of pressures at constant volume and temperature. As stated here, the law is simply a prescription for writing the equation of state of a gas mixture given the equations of the constituent gases. Recently the suggestion <sup>2</sup> has been made that Gibbs' <sup>3</sup> formulation of Dalton's law, which does contain the idea of equilibrium required as a basis for the thermodynamic treatment of gas mixtures, was implied by Dalton. Dalton did state that the same amount of a liquid would evaporate into air as into a vacuum. But his discussion was a kinetic one based on "no attractive or repulsive power" between the particles of different substances composing a gas mixture, so that the foregoing statement of his law, although not given in exactly his terms, seems to summarize Dalton's conclusion.

Consider a series of vessels, one containing a gas mixture and the others containing the pure constituent gases subject to the conditions:

$$\left. \begin{array}{ll} T(\text{each pure gas}) & T(\text{mixture}) \\ V(\text{each pure gas}) & V(\text{mixture}) \\ n_k = n_i, \text{ that is, } C_k = C_i & i \equiv k = 1, 2, \dots \end{array} \right\} \quad (\text{A})$$

Here the subscript  $i$  denotes one of the gases in the mixture,  $k$  the same gas when pure, and  $C$  the concentration,  $(n/V)$ . Dalton's law states

$$p = \sum_k p_{ck} \quad (8.1)$$

where  $p$  is the total pressure of the mixture and  $p_{ck}$  that of the constituent gas  $k$  measured pure and subject to the conditions (A). The subscript  $c$  indicates that concentration of the gas is the same in the pure state as in the mixture.

Dalton's law can be applied to real as well as ideal gases. It requires that the equation of state of a gas mixture be the sum

$$p = f_1(V, T, n_1) + f_2(V, T, n_2) + \dots \quad (8.2)$$

where  $p$  is the pressure of the mixture, and

$$p_{ck} = f_k(V, T, n_k) \quad (8.3)$$

is the equation of state of the pure gas  $k$ . Applied to the Equation (6.1)

<sup>1</sup> J. Dalton, *Nicholson's J. of Natural Phil.*, 5, 241 (1801); *Gilbert's Ann. Phys.*, 12, 385 (1802); *ibid.*, 15, 1 (1803).

<sup>2</sup> L. J. Gillespie, *Phys. Rev.*, 36, 121 (1930).

<sup>3</sup> J. W. Gibbs, *Scientific Papers*, Vol. I (New York: Longmans, Green and Co., 1906), pp. 155-157.



Dalton's law gives

$$p = \frac{(\sum_i n_i)RT}{V} + (\sum_i x_i^2 \beta_i) \frac{(\sum_i n_i)^2}{V^2} + (\sum_i x_i^3 \gamma_i) \frac{(\sum_i n_i)^3}{V^3} + (\sum_i x_i^4 \delta_i) \frac{(\sum_i n_i)^4}{V^4} \quad (8.4)$$

where  $\beta_i$ ,  $\gamma_i$ ,  $\delta_i$  are the virial parameters for the pure gas  $k$ . At low pressures the law gives good results, but at higher pressures the errors may become very large.

From a study of his measurements of the compressibilities of oxygen, nitrogen, and air Amagat<sup>4</sup> concluded that: The volume of a mixture of gases is equal to the sum of the volumes of the different gases as existing each by itself at the temperature and under the total pressure of the mixture. This is the law of the additivity of volumes at constant pressure and temperature.

Consider a gas mixture and the pure constituents each measured under the conditions

$$\left. \begin{aligned} T(\text{each pure gas}) &= T(\text{mixture}) \\ p(\text{each pure gas}) &= p(\text{mixture}) \\ n_k &= n_i \quad i \equiv k = 1, 2, \dots \end{aligned} \right\} \quad (B)$$

Amagat's law requires

$$V = \sum_k V_{Pk} \quad (8.5)$$

where  $V$  is the volume of the mixture and  $V_{Pk}$  that of the pure gas  $k$  measured under the conditions (B).

Amagat's law gives for the volume  $V$  of a mixture the relation

$$V = F_1(p, T, n_1) + F_2(p, T, n_2) + \dots \quad (8.6)$$

where

$$V_k = F_k(p, T, n_k) \quad (8.7)$$

is the equation of state of the pure gas  $k$ . Thus for a gas mixture obeying Amagat's law Equation (6.3) becomes

$$V = \frac{(\sum_i n_i)RT}{p} + \frac{(\sum_i n_i \beta_i)}{RT} + \frac{(\sum_i n_i \gamma_i)}{(RT)^2} p + \frac{(\sum_i n_i \delta_i)}{(RT)^3} p^2 \quad (8.8)$$

Amagat's law gives, in general, a better representation of the properties of gas mixtures than Dalton's law, although there are some notable exceptions. At least Amagat's law gives the correct result for the mixing of a gas with itself whereas Dalton's law does not.

(9) **Equation of State of Gas Mixtures:** The  $n$ -th virial coefficient of the complete expansion of  $pv$  for a binary gas mixture has been shown<sup>1</sup> from statistical mechanics to be a polynomial of the  $n$ -th order in the mole fractions, the coefficients being function of the temperature. Thus the second, third, and

<sup>4</sup> E. H. Amagat, *Ann. chim. phys.*, (5), 19, 384 (1880); *Compt. rend.*, 127, 88 (1898).

<sup>1</sup> J. E. Mayer, *J. Phys. Chem.*, 43, 71 (1939).

fourth virial coefficients of a binary mixture would be written

$$\beta_m = \sum_i \sum_j x_i x_j \beta_{ij} \quad (9.1)$$

$$\gamma_m = \sum_i \sum_j \sum_k x_i x_j x_k \gamma_{ijk} \quad (9.2)$$

$$\delta_m = \sum_i \sum_j \sum_k \sum_l x_i x_j x_k x_l \delta_{ijkl} \quad (9.3)$$

The subscript  $m$  denotes the value of a quantity for the mixture. Quantities on the right with all subscripts the same refer to the pure components, otherwise to interaction parameters arising from collisions of unlike molecules. For a binary mixture the second virial coefficient becomes

$$\beta_m = x_1^2 \beta_{11} + 2x_1 x_2 \beta_{12} + x_2^2 \beta_{22} \quad (9.4)$$

since the two interaction constants are obviously equal:

$$\beta_{12} = \beta_{21} \quad (9.5)$$

We might well generalize Equations (9.1) to (9.3) and apply them to a mixture of any number of components.<sup>2</sup> Thus for a ternary gas mixture Equation (9.4) would be written

$$\beta_m = x_1^2 \beta_{11} + x_2^2 \beta_{22} + x_3^2 \beta_{33} + 2x_1 x_2 \beta_{12} + 2x_1 x_3 \beta_{13} + 2x_2 x_3 \beta_{23} \quad (9.6)$$

From the relation between the second virial coefficients and the equation of state constants, Equation (6.1), we would conclude that Equation (9.1) gives the dependence of the constants  $A_{0m}$ ,  $B_{0m}$ , and  $c_m$  of a gas mixture on the composition, and we might extend the same method of computation to the less important parameters  $a_m$  and  $b_m$ . The interaction coefficients, as  $A_{0ij}$ , are now constants characteristic of the pair of gases  $i$  and  $j$ . The foregoing method does not yet yield an equation of state of gas mixtures as defined in Section 1 since the method of computing the interaction constants, except from data on gas mixtures, is not defined.

Several methods of computing the values of the interaction constants from the corresponding constants of the pure gases have been proposed. Let  $B$  represent any one of the equation of state constants. Then the most used relations<sup>3</sup> for combination of constants are

$$B_{ij} = \frac{1}{2}(B_{ii} + B_{jj}) \quad (\text{linear combination}) \quad (9.7)$$

$$B_{ij} = B_{ii}^{1/2} B_{jj}^{1/2} \quad (\text{square-root combination}) \quad (9.8)$$

$$B = \left( \frac{B_{ii}^{1/3} + B_{jj}^{1/3}}{2} \right)^3 \quad (\text{Lorentz combination}) \quad (9.9)$$

The first relation gives the largest value of  $B_{ij}$ , and the second the smallest. The following tabulation gives an idea of the magnitudes of the differences encountered for several ratios of  $B_{ij}$  to  $B_{ii}$ .

<sup>2</sup> K. Fuchs, *Proc. Roy. Soc. (London)*, **A179**, 408 (1941).

<sup>3</sup> J. D. van der Waals, *Die Continuität des gasförmigen and flüssigen Zustandes*, Barth, Leipzig (1899–1900); H. A. Lorentz, *Ann. Physik*, **12**, 127, 660 (1881); B. Galitzine, *Ann. Physik*, **41**, 770 (1890); D. Berthelot, *Compt. rend.*, **126**, 1703, 1857 (1898).

VALUES OF  $B_{ij}$ 

		Linear $B_{ij}$	Square-Root $B_{ij}$	Lorentz $B_{ij}$
$B_{ij}$	$1.1B_{ii}$	$1.0500B_{ii}$	$1.0488B_{ii}$	$1.0492B_{ii}$
$B_{ij}$	$2.0B_{ii}$	$1.5000B_{ii}$	$1.4142B_{ii}$	$1.4427B_{ii}$
$B_{ij}$	$4.0B_{ii}$	$2.5000B_{ii}$	$2.0000B_{ii}$	$2.1652B_{ii}$
$B_{ij} = 10.0B_{ii}$		$5.500B_{ii}$	$3.162B_{ii}$	$3.924B_{ii}$

General physical considerations indicate square-root combination for the attractive constant  $A_0$  ( $a$  of van der Waals' equation) and Lorentz combination for the repulsive constant  $B_0$  ( $b$  in van der Waals' equation). The latter corresponds to averaging the radii of the molecules. The best representation of the compressibilities of gas mixture is obtained <sup>4</sup> by square-root combination for  $c$ , provided Lorentz combination is used for  $B_0$ ; but the much simpler linear-combination for both  $B_0$  and  $c$  gives quite satisfactory results.

Thus we shall write for the interaction constants

$$\left. \begin{aligned} A_{0ij} &= A_{0ii}^{1/2} A_{0jj}^{1/2} & a_{ij} &= \frac{a_{ii} + a_{jj}}{2} \\ B_{0ij} &= \left( \frac{B_{0ii}^{1/3} + B_{0jj}^{1/3}}{2} \right)^3 & b_{ij} &= \frac{b_{ii} + b_{jj}}{2} \\ c_{ij} &= c_{ii}^{1/2} c_{jj}^{1/2} \end{aligned} \right\} \quad (9.10)$$

The parameters for a gas mixture are

$$\left. \begin{aligned} A_{0m} &= \sum_i \sum_j x_i x_j A_{0ii}^{1/2} A_{0jj}^{1/2} \\ a_m &= \sum_i \sum_j x_i x_j \frac{a_{ii} + a_{jj}}{2} \\ B_{0m} &= \sum_i \sum_j x_i x_j \left( \frac{B_{0ii}^{1/3} + B_{0jj}^{1/3}}{2} \right)^3 \\ b_m &= \sum_i \sum_j x_i x_j \left( \frac{b_{ii} + b_{jj}}{2} \right) \\ c_m &= \sum_i \sum_j x_i x_j c_{ii}^{1/2} c_{jj}^{1/2} \end{aligned} \right\} \quad (9.11)$$

We can now write Equation (6.1) as an equation of state for gas mixtures.

$$p = \frac{(\sum_i n_i)RT}{V} + \frac{(\sum_i n_i)^2 \beta_r}{V^2} + \frac{(\sum_i n_i)^3 \gamma_m}{V^3} + \frac{(\sum_i n_i)^4 \delta_m}{V^4} \quad (9.12)$$

where

$$\left. \begin{aligned} \beta_m &= RTB_{0m} - A_{0m} - \frac{Rc_m}{T^2} \\ \gamma_m &= -RTB_{0m}b_m + A_{0m}a_m - \frac{RB_{0m}c_m}{T^2} \\ \delta_m &= \frac{RB_{0m}b_m c_m}{T^2} \end{aligned} \right\} \quad (9.13)$$

and:

$$\begin{aligned}
 A_{0m} &= (\sum_i x_i A_{0i}^{1/2})^2 \\
 B_{0m} &= \frac{1}{8} \sum_i \sum_j x_i x_j (B_{0i}^{1/3} + B_{0j}^{1/3})^3 = \frac{1}{4} (\sum_i x_i B_{0i}) + \frac{3}{4} (\sum_i x_i B_{0i}^{1/3}) (\sum_i x_i B_{0i}^{2/3}) \\
 c_m &= (\sum_i x_i c_i^{1/2})^2 \\
 a_m &= (\sum_i x_i a_i) \\
 b_m &= (\sum_i x_i b_i)
 \end{aligned} \tag{9.14}$$

In the foregoing equations  $A_{0i}$  has been written for  $A_{0ii}$  and similarly for the other constants since no confusion is introduced.

The equation of state for gas mixtures explicit in the volume is

$$\frac{V}{(\sum_i n_i)} = \frac{RT}{p} + \frac{\beta_m}{RT} + \frac{\gamma_m}{(RT)^2} p + (RT) p^2 \tag{9.15}$$

and the approximate mixture relation similar to Equation (6.5) for pure gases becomes

$$\frac{V}{(\sum_i n_i)} = \frac{RT}{p} + \frac{\beta_m}{RT} \tag{9.16}$$

The combination of constants rules of Equation (9.11) violates in two instances the relations (9.2) and (9.3). In  $\gamma_m$  the term  $RB_{0m}c_m/T^2$  is of the fourth degree in the mole fractions; and the term  $\delta_m$ ,  $RB_{0m}b_m c_m/T^2$ , is of the fifth degree. To overcome this difficulty we might consider  $B_{0m}c_m$  as a single rather than a composite constant and write

$$(B_{0m}c_m) = [\sum_i (B_{0i}c_i)^{1/3}]^3 \tag{9.17}$$

However, the difference between this and the method of Equation (9.14) is unimportant in the calculation of  $p$  or  $(\partial p/\partial n_i)_{VTn}$  from Equation (9.12), or of  $V$  or  $(\partial V/\partial n_i)_{pTn}$  from Equation (9.15).

**(10) Derivatives of the Equation of State Parameters:** The temperature derivatives of the virial parameters  $\beta$ ,  $\gamma$ ,  $\delta$  of Equation (6.1) are

$$\begin{aligned}
 \frac{d\beta}{dT} &= RB_0 + \frac{2Rc}{T^3} & \frac{d^2\beta}{dT^2} &= -\frac{6Rc}{T^4} \\
 \frac{d\gamma}{dT} &= -RB_0b + \frac{2RB_0c}{T^3} & \frac{d^2\gamma}{dT^2} &= -\frac{6RB_0c}{T^4} \\
 \frac{d\delta}{dT} &= -\frac{2RB_0bc}{T^3} & \frac{d^2\delta}{dT^2} &= \frac{6RB_0bc}{T^4}
 \end{aligned} \tag{10.1}$$

The temperature derivatives at constant composition of the parameters of the Equations (9.12), (9.15), and (9.16) for gas mixtures are given by the relations (10.1) with the constants of the pure gas replaced by the parameters of the particular mixture:  $\beta_m$ ,  $\gamma_m$ ,  $\delta_m$ , and  $A_{0m}$ ,  $B_{0m}$ ,  $c_m$ ,  $a_m$ ,  $b_m$ .

The derivatives of the equation of state parameters of a mixture with respect to one of the mole numbers  $n_i$  with all of the other mole numbers held constant (denoted by a subscript  $n$  to the partial derivative) are

$$\begin{aligned}
 \left( \frac{\partial B_{0m}}{\partial n_i} \right)_n &= \frac{1}{(\Sigma_i n_i)} [B_{0i} + D_i(B_0) - B_{0m}]; \\
 D_i(B_0) &= -\frac{3}{4}(B_{0i}^{1/3} - \Sigma_i x_i B_{0i}^{1/3})(B_{0i}^{2/3} - \Sigma_i x_i B_{0i}^{2/3}) \\
 \left( \frac{\partial A_{0m}}{\partial n_i} \right)_n &= \frac{1}{(\Sigma_i n_i)} [A_{0i} + D_i(A_0) - A_{0m}]; \\
 D_i(A_0) &= -(A_{0i}^{1/2} - \Sigma_i x_i A_{0i}^{1/2})^2 \\
 \left( \frac{\partial c_m}{\partial n_i} \right)_n &= \frac{1}{(\Sigma_i n_i)} [c_i + D_i(c) - c_m]; \\
 D_i(c) &= -(c_i^{1/2} - \Sigma_i x_i c_i^{1/2})^2 \\
 \left( \frac{\partial a_m}{\partial n_i} \right)_n &= \frac{1}{(\Sigma_i n_i)} [a_i - a_m] \\
 \left( \frac{\partial b_m}{\partial n_i} \right)_n &= \frac{1}{(\Sigma_i n_i)} [b_i - b_m]
 \end{aligned} \tag{10.2}$$

The derivatives of the virial parameters with respect to  $n_i$  for use in Equations (9.12), (9.15), and (9.16) are

$$\left. \begin{aligned}
 \left( \frac{\partial \beta_m}{\partial n_i} \right)_{Tn} &= \frac{2}{(\Sigma_i n_i)} [\Sigma_j x_j \beta_{ij} - \beta_m] \\
 &\quad \frac{1}{(\Sigma_i n_i)} [\beta_i + D_i(\beta) - \beta_m] \\
 \left( \frac{\partial \gamma_m}{\partial n_i} \right)_{Tn} &= \frac{3}{(\Sigma_i n_i)} [\Sigma_j \Sigma_k x_j x_k \gamma_{ijk} - \gamma_m] \\
 &\quad \frac{1}{(\Sigma_i n_i)} [\gamma_i + D_i(\gamma) - 2\gamma_m] \\
 \left( \frac{\partial \delta_m}{\partial n_i} \right)_{Tn} &= \frac{4}{(\Sigma_i n_i)} [\Sigma_j \Sigma_k \Sigma_l x_j x_k x_l \delta_{ijkl} - \delta_m] \\
 &\quad \frac{1}{(\Sigma_i n_i)} [\delta_i + D_i(\delta) - 3\delta_m] \\
 D_i(\beta) &= RTD_i(B_0) - D_i(A_0) - \frac{R}{T^2} D_i(c) \\
 &\quad - \frac{3RT}{4} (B_{0i}^{1/3} - \Sigma_i x_i B_{0i}^{1/3})(B_{0i}^{2/3} - \Sigma_i x_i B_{0i}^{2/3}) \\
 &\quad + (A_{0i}^{1/2} - \Sigma_i x_i A_{0i}^{1/2})^2 + \frac{R}{T^2} (c_i^{1/2} - \Sigma_i x_i c_i^{1/2})^2
 \end{aligned} \right\} \tag{10.3}$$

Equation (10.3) continued on next page.

$$\begin{aligned}
D_i(\gamma) = & -RT\{b_m[B_{0i} + D_i(B_0)] + b_i[B_{0m} - B_{0i}]\} \\
& + \{a_m[A_{0i} + D_i(A_0)] + a_i[A_{0m} - A_{0i}]\} \\
& - \frac{R}{T^2} \{c_m[B_{0i} + D_i(B_0)] + c_i[B_{0m} - B_{0i}] + B_{0m}D_i(c)\} \\
D_i(\delta) = & \frac{R}{T^2} \{B_{0m}b_m[c_i + D_i(c)] + b_m c_m[B_{0i} + D_i(B_0)] \\
& + b_i[B_{0m}c_m - B_{0i}c_i]\}
\end{aligned}$$

To determine the derivative with respect to  $n_i$  of the product of any parameter (say  $\beta_m$ ) into  $(\Sigma_i n_i)$  raised to any power  $q$ , we can use

$$\left( \frac{\partial [(\Sigma_i n_i)^q \beta_m]}{\partial n_i} \right)_{T_n} = (\Sigma_i n_i)^q \left( \frac{\partial \beta_m}{\partial n_i} \right)_{T_n} + q(\Sigma_i n_i)^{q-1} \beta_m \quad (10.4)$$

The arrangement of the computation of the foregoing derivatives for ethane in one mixture of ethane and  $n$ -butane is given in Table III. This pair of substances was chosen because the equation of state constants of  $n$ -butane are about two to four times as large as those of ethane. The method is evidently applicable to mixtures of any number of constituents.

Two quantities of importance in the theory of gas mixtures are the partial molar volume,  $(\partial V / \partial n_i)_{pT_n}$ , and the corresponding quantity  $(\partial p / \partial n_i)_{VT_n}$ .

From the equation of state of gas mixtures (9.15) explicit in the volume and the relations (10.3) and (10.4) we find

$$\begin{aligned}
\left( \frac{\partial V}{\partial n_i} \right)_{pT_n} = & \frac{RT}{p} + \frac{[\beta_i + D_i(\beta)]}{RT} + \frac{[\gamma_i + D_i(\gamma) - \gamma_m]}{(RT)^2} p \\
& + \frac{[\delta_i + D_i(\delta) - 2\delta_m]}{(RT)^3} p^2 \quad (10.5)
\end{aligned}$$

$$\begin{aligned}
\frac{V_{Pk}}{n_k} + \frac{D_i(\beta)}{RT} + \frac{[D_i(\gamma) - \gamma_m]}{(RT)^2} p + \frac{[D_i(\delta) - 2\delta_m]}{(RT)^3} p \\
(i \equiv k = 1, 2, \dots) \quad (10.6)
\end{aligned}$$

The term  $V_{Pk}/n_k$  is molar volume of gas  $i$  measured pure at the total pressure and the temperature of the mixture. It is the value of the partial molar volume predicted by Amagat's law, see Equations (8.5) and (8.8). For the gas mixture considered in Table III we find for the ethane in the mixture

$$\left( \frac{\partial V}{\partial n_i} \right)_{pT_n} - \frac{V_{Pk}}{n_k} = 0.01530 - 4.30 \times 10^{-5} p - 7.6 \times 10^{-8} p^2 \quad (10.7)$$

where  $p$  is in atmospheres and  $V$  in liters, and the values of the constants appropriate for the equation of state explicit in the pressure were used. The calculated value of the right-hand side of Equation (10.7) is 0.014 liter per mole, for a volume of 1 liter per mole. The computed error of Amagat's law is 1.4 per cent, a small error for this pressure, 36.59 atm.

TABLE III

COMPUTATION OF THE DERIVATIVES OF THE VIRIAL PARAMETERS WITH RESPECT TO MOLE NUMBERS FOR A GAS MIXTURE

See Equations (10.3) and (10.4).

Units: atmosphere, liter per mole, degree Kelvin.  $R = 0.08206$ .The calculation is made for ethane in a gas mixture 50 mole per cent ethane and 50 mole per cent *n*-butane at 500°K. $Y$  represents any parameter in the columns following.

	$A_0$	$B_0$	$10^{-4} \times c$	$a$	$b$	$A_0^{1/2}$	$B_0^{1/2}$	$B_0^{2/3}$	$10^{-2} \times c^{1/2}$
$Y_1(\text{ethane})$ .....	5.8800	0.09400	90.00	0.05861	0.01915	2.42487	0.454684	0.206738	9.4868
$Y_2(n\text{-butane})$ .....	17.7940	0.24620	350.00	0.12161	0.09423	4.21829	0.626752	0.392818	18.7083
$\sum_{i \neq 1} x_i Y_i$ .....		0.170100		0.0901100	0.0566900	3.32158	0.540718	0.299778	14.0976
$Y_m(\text{mixture})$ .....	11.03289	0.164097	198.742	0.0901100	0.0566900				
$Y_1 - \sum_{i \neq 1} x_i Y_i$ .....						-0.89671	-0.086034	-0.093040	-4.6108
$D_1(Y)$ .....	-0.80409	-0.006003	- 21.259						
$Y_1 + D_1(Y)$ .....	+5.07591	+0.087997	+ 68.741						
$Y_m - Y_1$ .....	+5.15289	+0.070097	+108.742						

	$\beta$	$\gamma$	$10^4 \times \delta$
$Y_1(\text{ethane})$ .....	-2.31860	+0.24300	+ 5.3178
$Y_m(\text{mixture})$ .....	-4.95234	+0.50544	+ 60.6860
$D_1(Y)$ .....	+0.62757	+0.43298	+ 68.7150
$Y_1 + D_1(Y)$ .....	-1.69103	+0.67598	+ 74.0328
$Y_1 + D_1(Y) + Y_m$ .....	-6.64337	+1.18142	+134.7188

Pressure of ethane at  $V = 1$  liter/mole from Equation (6.1) = 38.95 atmPressure of mixture at  $V = 1$  liter/mole from Equation (9.12) = 36.59 atm

Equation (9.12) and the partial derivatives listed above give

$$\begin{aligned}
 \left( \frac{\partial p}{\partial n_i} \right)_{VTn} &= \frac{RT}{V} + [\beta_i + D_i(\beta) + \beta_m] \frac{(\sum_i n_i)}{V^2} \\
 &\quad + [\gamma_i + D_i(\gamma) + \gamma_m] \frac{(\sum_i n_i)^2}{V^3} \\
 &\quad + [\delta_i + D_i(\delta) + \delta_m] \frac{(\sum_i n_i)^3}{V^4} \quad (10.8) \\
 &= \left( \frac{\partial p_{ck}}{\partial n_k} \right)_{VTn_k} + [\beta_i(1 - 2x_i) + D_i(\beta) + \beta_m] \frac{(\sum_i n_i)}{V^2} \\
 &\quad + [\gamma_i(1 - 3x_i^2) + D_i(\gamma) + \gamma_m] \frac{(\sum_i n_i)^2}{V^3} \\
 &\quad + [\delta_i(1 - 4x_i^3) + D_i(\delta) + \delta_m] \frac{(\sum_i n_i)^3}{V^4} \\
 &\quad (i \equiv k = 1, 2, \dots) \quad (10.9)
 \end{aligned}$$

The term  $(\partial p_{ck}/\partial n_k)_{VTn_k}$  is the value of  $(\partial p/\partial n_i)_{VTn}$  given by Dalton's law, see Equations (8.1) and (8.4), and the sum of the remaining terms on the right-hand side of Equation (10.9) is the error of the Dalton law calculation. For the ethane in the mixture considered in Table III at 500°K and a volume of 1 liter per mole, the value of  $(\partial p/\partial n_i)_{VTn}$  computed from Equation (10.8) is 35.58 atm per mole of ethane and the Dalton value,  $(\partial p_{ck}/\partial n_k)_{VTn_k}$ , is 38.89 atm per mole of ethane, an error of 9.3 per cent. For this mixture and under the specified conditions, Amagat's law is considerably better than Dalton's law.

(11) **Other Rules for Combination of Constants:** Application <sup>1,2</sup> of the relation for the second virial coefficient given by the Lennard-Jones potential to gas mixtures indicates that the interaction constants  $\sigma_{12}$  and  $\theta_{12}$  of Equation (3.17) should be combined according to the rules:

$$\begin{aligned}
 \sigma_{12} &= \frac{1}{2}(\sigma_{11} + \sigma_{22}) \\
 \theta_{12} &= \theta_{11}^{1/2} \theta_{22}^{1/2} \quad (11.1)
 \end{aligned}$$

Since  $B_0$  of the equation of state is analogous to  $2\pi N_0 \sigma^3/3$  and  $A_0/RB_0$  to  $\theta$ , the foregoing methods for the computation of the interaction constants suggest<sup>3</sup> that the second virial coefficient of a gas mixture be written

$$\frac{\beta_m}{RT} = B_{0m} \left[ 1 - \left( \frac{A_0}{B_0} \right)_m \frac{1}{RT} - \left( \frac{c}{B_0} \right)_m \frac{1}{T^3} \right] \quad (11.2)$$

and that  $B_{0m}$  be computed by Lorentz combination as in Equation (9.11) but

<sup>1</sup> J. E. Lennard-Jones and W. R. Cook, *Proc. Roy. Soc. (London)*, **A115**, 334 (1927).

<sup>2</sup> J. O. Hirschfelder and W. E. Roseveare, *J. Phys. Chem.*, **43**, 15 (1939).

<sup>3</sup> J. A. Beattie and W. H. Stockmayer, *J. Chem. Phys.*, **10**, 473 (1942).



that the ratios  $(A_0/B_0)_m$  and  $(c/B_0)_m$  be combined by square-root combination, as for  $A_{0m}$  in Equation (9.11).

Equation (5.8) gives a relation for the second virial coefficient  $B$  of a highly polar gas, as water vapor:

$$B = B_0 - \frac{A}{RT} e^{D/T^2} \quad (11.3)$$

In the application<sup>4</sup> of this relation to mixtures containing polar gases, the constants  $A$  and  $D$  are each written as the sum of two terms: one,  $A_0$  and  $D_0$ , depending on the type of intermolecular force common to all kinds of molecules; and the second,  $A_p$  and  $D_p$ , on the dipole moment  $\mu$  and differing from zero only if the molecules are polar:

$$\left. \begin{aligned} A &= A_0 + A_p \\ D &= D_0 + D_p \end{aligned} \right\} \quad (11.4)$$

$$\left. \begin{aligned} A_0 &= \frac{1}{2}[A + (A^2 - 0.756\mu^4)^{1/2}] \\ A_p &= \frac{1}{2}[A - (A^2 - 0.756\mu^4)^{1/2}] \end{aligned} \right\} \quad (11.5)$$

$$\left. \begin{aligned} D_0 &= D - D_p \\ D_p &= 13.6\mu^4/B_0^2 \end{aligned} \right\} \quad (11.6)$$

In case the form (11.3) has not been fitted to the experimental data for non-polar gases in the mixture, we can write  $D_0 = Rc/A_0$  for these gases (compare Equations [5.9] and [5.6]). For gas mixtures,  $B_{0m}$  is computed by Lorentz combination, and  $A_{0m}$ ,  $A_{pm}$ ,  $D_{0m}$ , and  $D_{pm}$  by square-root combination. In the above relations the units of the equation of state are atmosphere, liter per mole, °K, and  $\mu$  is in Debye units.

#### THERMODYNAMIC TREATMENT OF PURE GASES

(12) **The General Limit Method:** The first and second laws of thermodynamics define the increase in the energy and entropy of a system that has undergone a change in state but not the absolute values of these quantities. We are at liberty to assign any value to the energy and entropy integration constants consistent with the particular problem to be solved. Some one state of each of the substances composing a system may be selected, and appropriate values may be assigned to the energy and entropy of the substance in this state. The state is called the standard state, and each substance has at each temperature a series of standard states.

One method applicable to gases is to select a single standard state for each substance, say the state of one mole at the pressure  $p_0$  and temperature  $T_0$ , the corresponding molar volume being  $v_0$ . Let the molar energy and entropy of the substance be  $E(p_0, T_0)$  and  $S(p_0, T_0)$  in this state. The problem of computing the energy and entropy of the pure gas in any other state  $(p, T)$  or

<sup>4</sup> W. H. Stockmayer, *J. Chem. Phys.*, 9, 863 (1941).

$(v, T)$  relative to the values in the standard state  $(p_0, T_0)$  or  $(v_0, T_0)$  is a simple one involving a two-step process: first integrating  $dE$  and  $dS$  from  $T_0$  to  $T$  at the constant pressure  $p_0$  [or the corresponding constant volume  $v_0$ ] and then integrating from  $p_0$  to  $p$  [or from  $v_0$  to  $v$ ] at the constant temperature  $T$ .

The only data required for carrying out the calculations to a numerical solution are: the value of the constant pressure heat capacity at  $p_0$  [or the constant volume heat capacity at  $v_0$ ] as a function of temperature; the compressibility of the gas at the temperature  $T$ , which may be given in the form of an equation of state or an equivalent table or graph; and the values of the integration constants  $E(p_0, T_0)$  and  $S(p_0, T_0)$ . Thus the problem is completely solved without the necessity of making any assumptions.

We cannot even get a start on a general thermodynamic theory of gas mixtures including mixtures in which chemical reactions may occur without some assumption regarding equilibrium between a gas mixture and its pure constituents. Amagat's law, Dalton's law, and an equation of state for gas mixtures do not contain the fundamental idea of equilibrium and hence are of no help. A number of approaches to the solution of the problem have been suggested and will be considered later. Of these the general limit method<sup>1</sup> yields equations for the thermodynamic properties of mixtures of real gases that may be considered exact. The method assumes<sup>2</sup> that as the pressure on a gaseous mixture approaches zero a certain property of the mixture approaches that of mixtures of ideal gases in a specified manner. The resulting equations express the thermodynamic properties of gas mixtures in terms of definite integrals that can be evaluated from an equation of state of mixtures as defined in Section 1 and from relations for the temperature variation of the constant volume heat capacity at zero pressure for the pure constituent gases. Thus no data on mixtures are required, although when available they may be employed in principle to evaluate the definite integrals by graphical means.

A similar method may be used to derive general relations for the thermodynamic properties of pure gases. The resulting equations contain a definite integral that can be evaluated by an equation of state or an equivalent graphical method. Two basic assumptions suffice for both pure gases and gas mixtures; but for clarity of presentation we shall separate the discussion of pure gases from that for mixtures. In this case we need three assumptions, two for pure gases and one for mixtures, one of the former being derivable from the other two.

(13) **Assumptions for Pure Gases:** We<sup>1</sup> shall consider two pressure regions:

(a) The region of low pressures, in which terms of the order of  $p^2$  are negligible in comparison with terms of the order of  $p$  or of unity.

(b) The region of very low pressures, in which terms of the order of  $p$  are

<sup>1</sup> L. J. Gillespie, *Chem. Revs.*, **18**, 359 (1936).

<sup>2</sup> L. J. Gillespie, *J. Am. Chem. Soc.*, **47**, 305 (1925); T. de Donder, *Compt. rend.*, **180**, 1922 (1925); J. A. Beattie, *Phys. Rev.*, **36**, 132 (1930).

<sup>1</sup> Much of the following treatment is taken from J. A. Beattie, *Chem. Rev.*, **44**, 141-192 (1949), and is reproduced with the permission of the publisher: The Williams and Wilkins Company, Baltimore.

negligible in comparison with unity. Thermodynamic quantities in the region of very low pressures will be denoted by a superscript asterisk, as  $p^*$ .

The two assumptions for pure gases are:

(a) At all temperatures <sup>2</sup> the pressure-volume product  $pV$  of a fixed mass  $m$  of a real gas at a constant temperature  $T$  and in the region of low pressure can be represented by the expression:

$$pV = F(T, m) + A(T, m)p + O(p^2) \quad (T, m \text{ constant}) \quad (13.1)$$

where the functions of temperature and mass,  $F(T, m)$  and  $A(T, m)$ , and their derivatives with respect to temperature are bounded, and  $O(p^2)$  represents terms of the order of  $p^2$ .

(b) At all temperatures the heat content  $H$  of a fixed mass of a gas at constant temperature and in the region of low pressures can be represented by the expression:

$$H = f(T, m) + B(T, m)p + O(p^2) \quad (T, m \text{ constant}) \quad (13.2)$$

where  $f(T, m)$  and  $B(T, m)$  and their derivatives with respect to temperature are bounded.

(14) **Results Derivable from the Assumptions:** Substitution from Equations (13.1) and (13.2) into the general thermodynamic relation

$$\left(\frac{\partial H}{\partial p}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_p \quad (m = \text{constant})$$

gives

$$B + O(p) = \frac{1}{p} \left[ F - T \left( \frac{\partial F}{\partial T} \right)_m \right] + \left[ A - T \left( \frac{\partial A}{\partial T} \right)_m \right] + O(p) \quad (m = \text{constant}) \quad (14.1)$$

for a fixed mass of gas in the region of low pressure. Equation (14.1) can hold for all values of the pressure in the region of low pressure only when

$$F - T \left( \frac{\partial F}{\partial T} \right)_m = 0 \quad (14.2)$$

Integration gives

$$F = r(m)T \quad (14.3)$$

where  $T$  is absolute thermodynamic temperature and  $r(m)$  depends only on the mass for any given gas. Thus Equation (13.1) becomes

$$pV = r(m)T + A(T, m)p + O(p^2) \quad (m \text{ constant}) \quad (14.4)$$

and in the region of very low pressures

$$(pV)^* = r(m)T \quad (m \text{ constant}) \quad (14.5)$$

<sup>2</sup> The region in the neighborhood of 0°K is to be excluded.

The volume is an extensive state property of a system. At constant pressure and temperature it is a homogeneous function of the first degree in the mass. If we replace  $V$  in Equation (14.5) by  $V/m$ , the volume per unit mass, the quantity  $r(m)$  will be a constant characteristic of each gas. Furthermore let  $m$  be expressed in terms of the mass unit: the mole. One mole of any gas is defined as the mass that occupies at a very low pressure and at each temperature the same volume as 32 grams of gaseous oxygen measured at the same pressure and temperature. When the mass of gas is expressed in moles,  $r$  is a universal constant independent of the kind of gas and is denoted by  $R$ . Thus for low pressures we may write Equation (14.4) in the form:

$$pV = nRT + \frac{n\beta p}{RT} + O(p^2) \quad (14.6)$$

and to the same degree of approximation

$$pV = nRT + \frac{n^2\beta}{V} + O\left(\frac{n}{V}\right)^2 \quad (14.7)$$

where  $n$  is the number of moles of gas in the volume  $V$ ,  $\beta$  is a pure temperature function and has the value

$$\beta = RTA(T, 1) \quad (14.8)$$

if  $A(T, 1)$  is taken for one mole of gas. The particular form used for  $\beta$  is chosen to conform to the usual method of writing equations of state.

**(15) The Path of Integration:** The standard state of each pure gaseous substance is one mole at any arbitrarily chosen pressure  $p_0$  and temperature  $T_0$ , the corresponding volume of  $n$  moles being  $V_0$ .

The thermodynamic functions in which we are interested are all state variables and hence we can proceed from the standard state  $(p_0, T_0)$  or  $(V_0, T_0)$  to any other state  $(p, T)$  or  $(V, T)$  along any path. We shall use a three-step path involving the region of very low pressure  $p^*$  where the corresponding volume is  $V^*$ . Let the number of moles  $n$  of gas remain constant and:

1. Change the pressure from  $p_0$  to  $p^*$  (or the volume from the corresponding values  $V_0$  to  $V^*$ ) at the temperature  $T_0$ .

2. Change the temperature from  $T_0$  to  $T$  with the pressure held constant at  $p^*$  (or the volume at  $V^*$ ).

3. Change the pressure from  $p^*$  to  $p$  (or the volume from  $V^*$  to  $V$ ) at the temperature  $T$ .

**(16) Derivations for the Independent Variables  $p$  and  $T$ :** The total differentials of the heat content  $H$  and entropy  $S$  of a constant mass of  $n$  moles of a real gas are:

$$dH = C_p dT + \left[ V - T \left( \frac{\partial V}{\partial T} \right)_p \right] dp \quad (16.1)$$

$$dS = \frac{C_p}{T} dT - \left( \frac{\partial V}{\partial T} \right)_p dp \quad (16.2)$$

where  $C_p$  is the constant pressure heat capacity of  $n$  moles. We can integrate these relations along the three-step path just described from the standard state  $(p_0, T_0)$  where the heat content and entropy have the values  $H(p_0, T_0)$  and  $S(p_0, T_0)$  to the variable state  $(p, T)$  and the corresponding values  $H(p, T)$  and  $S(p, T)$ :

$$H(p, T) - H(p_0, T_0) = \int_{T_0}^{p^*} \left[ V - T \left( \frac{\partial V}{\partial T} \right)_p \right] dp + \int_{p^*}^T n c_p^* dT + \int_T^p \left[ V - T \left( \frac{\partial V}{\partial T} \right)_p \right] dp \quad (16.3)$$

$$S(p, T) - S(p_0, T_0) = - \int_{T_0}^{p^*} \left( \frac{\partial V}{\partial T} \right)_p dp + \int_{p^*}^T \frac{n c_p^*}{T} dT - \int_T^p \left( \frac{\partial V}{\partial T} \right)_p dp \quad (16.4)$$

Here  $c_p^*$  is the molar constant pressure heat capacity of the gas in the region of very low pressure. Addition and subtraction of the term  $nR \ln (p/p_0)$  to the right-hand side of Equation (16.4) gives

$$S(p, T) - S(p_0, T_0) = \int_{T_0}^{p^*} \left[ \frac{nR}{p} - \left( \frac{\partial V}{\partial T} \right)_p \right] dp + \int_{p^*}^T \frac{n c_p^*}{T} dT + \int_T^p \left[ \frac{nR}{p} - \left( \frac{\partial V}{\partial T} \right)_p \right] dp - nR \ln \frac{p}{p_0} \quad (16.5)$$

These expressions can be simplified. From Equation (14.6) we find

$$\lim_{p^* \rightarrow 0} \int_{p^*}^0 \left[ V - T \left( \frac{\partial V}{\partial T} \right)_p \right] dp = \lim_{p^* \rightarrow 0} \left[ \left( T \frac{d\beta}{dT} - 2\beta \right) \frac{np^*}{RT} + O(p^{*2}) \right] = 0 \quad (16.6)$$

$$\lim_{p^* \rightarrow 0} \int_{p^*}^0 \left[ \frac{nR}{p} - \left( \frac{\partial V}{\partial T} \right)_p \right] dp = \lim_{p^* \rightarrow 0} \left[ \left( \frac{d\beta}{dT} - \frac{\beta}{T} \right) \frac{np^*}{RT} + O(p^{*2}) \right] = 0 \quad (16.7)$$

so that the limits  $p^*$  in Equations (16.3) and (16.5) can be replaced by zero.

From Equation (13.2) we see that

$$n c_p = \left( \frac{\partial H}{\partial T} \right)_{pn} = \left( \frac{\partial f}{\partial T} \right)_m + \left( \frac{\partial B}{\partial T} \right)_m p + O(p^2) \quad (16.8)$$

whence

$$n c_p^* = \left( \frac{\partial f}{\partial T} \right)_m \quad (16.9)$$

a pure temperature function.

Let us define the following quantities:

$$h^0 = h_0^0 + \int_{T_0}^T c_p^* dT \quad (16.10)$$

$$nh_0^0 = H(p_0, T_0) + \int_{T_0}^{T^*} \left[ V - T \left( \frac{\partial V}{\partial T} \right)_p \right] dp \quad (16.11)$$

$$s^0 = s_0^0 + \int_{T_0}^T \frac{c_p^*}{T} dT \quad (16.12)$$

$$ns_0^0 = S(p_0, T_0) + \int_{T_0}^{T^*} \left[ \frac{nR}{p} - \left( \frac{\partial V}{\partial T} \right)_p \right] dp + nR \ln p_0 \quad (16.13)$$

Equations (16.3) and (16.5) can now be written

$$H(p, T) = \int_0^p \left[ V - T \left( \frac{\partial V}{\partial T} \right)_p \right] dp + nh^0 \quad (16.14)$$

$$S(p, T) = \int_0^p \left[ \frac{nR}{p} - \left( \frac{\partial V}{\partial T} \right)_p \right] dp - nR \ln p + ns^0 \quad (16.15)$$

In view of Equation (16.14) we may interpret the parameter  $h^0$  in either of the following ways:

(a)  $h^0$  is the molar heat content of the gas at the temperature  $T$  and a very low pressure:

$$h^0 = \frac{1}{n} H(p^*, T) \quad (16.16)$$

(b)  $h^0$  is the molar heat content the gas would have at the temperature  $T$  and any pressure, say one atmosphere, if it behaved as an ideal gas, i.e., if  $V - T(\partial V/\partial T)_p = 0$ .

The corresponding interpretations of  $s^0$  from Equation (16.15) are:

(a)  $s^0$  is the molar entropy of the gas at the temperature  $T$  and a very low pressure increased by  $R \ln p^*$

$$s^0 = \frac{1}{n} S(p^*, T) + R \ln p^* \quad (16.17)$$

(b)  $s^0$  is the molar entropy the gas would have at the temperature  $T$  and one atmosphere pressure if it behaved as an ideal gas.

The quantities  $h_0^0$  and  $s_0^0$  have a similar interpretation for the standard state temperature  $T_0$ . They are constants characteristic of each gas. Their evaluation will be considered later.

We can now write the relations for the energy  $E$ , work content  $A$ , free energy  $F$ , chemical potential  $\mu$ , and fugacity  $f$  of a gas from the usual thermo-

dynamic relations:

$$H = E + pV \quad (16.18)$$

$$A = E - TS \quad (16.19)$$

$$F = H - TS \quad (16.20)$$

$$\mu = \left( \frac{\partial A}{\partial T} \right)_{V, T_n} = \left( \frac{\partial F}{\partial T} \right)_{p, T_n} \quad (16.21)$$

$$\mu = RT \ln f + h^0 - Ts^0 \quad (16.22)$$

The thermodynamic relation between the heat capacity at constant pressure  $C_p$  and the heat capacity at constant volume  $C_V$  is

$$C_p = C_V - T \frac{(\partial V / \partial T)_p^2}{(\partial V / \partial p)_T} \quad (16.23)$$

Evaluation of the partial derivatives from Equation (14.6) gives

$$C_p - C_V = nR + O(p) \quad (16.24)$$

whence

$$c_p^* = c_v^* + R \quad (16.25)$$

where  $c_p^*$  and  $c_v^*$  are the molar quantities in the region of very low pressure.

The relation

$$dC_p = -T \left( \frac{\partial^2 V}{\partial T^2} \right)_p dp \quad (T, n \text{ constant}) \quad (16.26)$$

can be integrated at constant temperature and mass from  $p^*$  to  $p$ :

$$C_p(p, T) - C_p^*(p^*, T) = -T \int_{p^*}^p \left( \frac{\partial^2 V}{\partial T^2} \right)_p dp \quad (16.27)$$

From Equation (14.6) we find that the limit  $p^*$  can be replaced by zero. Also  $C_p^*(p^*, T)$  is simply  $nc_p^*$ . Hence

$$C_p = nc_p^* - T \int_0^p \left( \frac{\partial^2 V}{\partial T^2} \right)_p dp \quad (16.28)$$

The corresponding relation for the variation of  $C_V$  with pressure is more complicated. This can be obtained, however, by computing  $C_p$  from Equation (16.28), then applying the relations (16.23) and (16.25) to convert  $C_p$  to  $C_V$  and  $c_p^*$  to  $c_v^*$ .

In the expression for the Joule-Thomson coefficient  $\mu_{J.T.}$

$$\mu_{J.T.} C_p = T^2 \left[ \frac{\partial(V/T)}{\partial T} \right]_p \quad (16.29)$$

$C_p$  is to be computed from Equation (16.28) and the partial derivative evaluated from an equation of state explicit in the volume, as Equation (6.2) or (6.3).

The relation for the Joule coefficient  $\eta$  may be written

$$\eta C_V = T \left( \frac{\partial p}{\partial T} \right)_V - p - \left[ p + T \left( \frac{\partial V / \partial T}{\partial V / \partial p} \right)_T \right] \quad (16.30)$$

All of the foregoing relations are collected in Section 18.

(17) **Derivations for the Independent Variables  $V$  and  $T$ :** The total differential of the energy  $E$  and entropy  $S$  of a constant mass of  $n$  moles of a real gas are

$$dE = C_V dT + \left[ T \left( \frac{\partial p}{\partial T} \right)_V - p \right] dV \quad (17.1)$$

$$dS = \frac{C_V}{T} dT + \left( \frac{\partial p}{\partial T} \right)_V dV \quad (17.2)$$

Integration from the standard state  $(V_0, T_0)$  to the variable state  $(V, T)$  along the three-step path gives

$$\begin{aligned} E(V, T) - E(V_0, T_0) &= \int_{T_0}^{V^*} \left[ T \left( \frac{\partial p}{\partial T} \right)_V - p \right] dV \\ &+ \int_{V^*}^T n c_v^* dT + \int_T^V \left[ T \left( \frac{\partial p}{\partial T} \right)_V - p \right] dV \end{aligned} \quad (17.3)$$

$$\begin{aligned} S(V, T) - S(V_0, T_0) &= \int_{T_0}^{V^*} \left( \frac{\partial p}{\partial T} \right)_V dV \\ &+ \int_{V^*}^T \frac{n c_v^*}{T} dT + \int_T^V \left( \frac{\partial p}{\partial T} \right)_V dV \end{aligned} \quad (17.4)$$

where  $c_v^*$  is the molar constant volume heat capacity in the region of very low pressures. Addition and subtraction of the term  $nR \ln V/V_0$  gives for Equation (17.4):

$$\begin{aligned} S(V, T) - S(V_0, T_0) &= \int_{T_0}^{V^*} \left[ \left( \frac{\partial p}{\partial T} \right)_V - \frac{nR}{V} \right] dV + \int_{V^*}^T \frac{n c_v^*}{T} dT \\ &+ \int_T^V \left[ \left( \frac{\partial p}{\partial T} \right)_V - \frac{nR}{V} \right] dV + nR \ln \frac{V}{V_0} \end{aligned} \quad (17.5)$$

We can simplify these expressions as before. Use of Equation (14.7) shows that

$$\lim_{V^* \rightarrow \infty} \int_{V^*}^{\infty} \left[ T \left( \frac{\partial p}{\partial T} \right)_V - p \right] dV = \lim_{V^* \rightarrow \infty} \int_{V^*}^{\infty} \left[ \left( \frac{\partial p}{\partial T} \right)_V - \frac{nR}{V} \right] dV = 0 \quad (17.6)$$

so that the limit  $V^*$  can be replaced by infinity.



From Equations (16.9) and (16.25) we find that  $c_v^*$  is a pure temperature function.

Let us define the following quantities:

$$e^0 = e_0^0 + \int_{T_0}^T c_v^* dT \quad (17.7)$$

$$ne_0^0 = E(V_0, T_0) + \int_{T_0}^{V^*} \left[ T \left( \frac{\partial p}{\partial T} \right)_v - p \right] dV \quad (17.8)$$

Now  $e^0$  and  $e_0^0$  can be related to  $h^0$  and  $h_0^0$ . From Equations (16.11), (17.8), and (14.6) we find

$$\begin{aligned} nh_0^0 - ne_0^0 &= H(p_0, T_0) - E(V_0, T_0) + \int_{T_0}^{p^*} \left[ V - T \left( \frac{\partial V}{\partial T} \right)_p \right] dp \\ &\quad - \int_{T_0}^{V^*} \left[ T \left( \frac{\partial p}{\partial T} \right)_v - p \right] dV \\ &= p_0 V_0 + \int_{T_0}^{p^*} \int_{p_0 V_0}^{V^*} d(pV) \\ &= nRT_0 \end{aligned} \quad (17.9)$$

This expression together with Equations (16.25), (16.10), and (17.7) gives

$$h^0 - e^0 = RT \quad (17.10)$$

Since  $S(V_0, T)$  refers to the same standard state as  $S(p_0, T_0)$ , we can replace the former in Equation (17.5) by the value of  $S(p_0, T_0)$  given by Equation (16.13). Thus on simplification we find for the following three terms of (17.5):

$$\begin{aligned} S(V_0, T_0) + \int_{T_0}^{V^*} \left[ \left( \frac{\partial p}{\partial T} \right)_v - \frac{nR}{V} \right] dV - nR \ln V_0 \\ = -nR \ln p_0 V_0 - nR \int_{T_0}^{p^*} \int_{p_0 V_0}^{V^*} d \ln(pV) + ns_0^0 \\ = -nR \ln nRT_0 + ns_0^0 \end{aligned} \quad (17.11)$$

Note that we can express  $s^0$  in terms of  $c_v^*$  rather than in terms of  $c_p^*$ :

$$s^0 = s_0^0 + \int_{T_0}^T \frac{c_v^*}{T} dT + R \ln \frac{T}{T_0} \quad (17.12)$$

Introduction of these simplifications into Equations (17.3) and (17.5) gives

$$E(V, T) = \int_V^\infty \left[ p - T \left( \frac{\partial p}{\partial T} \right)_v \right] dV + ne^0 \quad (17.13)$$

$$S(V, T) = \int_V^\infty \left[ \frac{nR}{V} - \left( \frac{\partial p}{\partial T} \right)_v \right] dV + nR \ln \frac{V}{nRT} + ns^0 \quad (17.14)$$

These, together with Equations (16.18) through (16.22), yield expressions for the thermodynamic properties  $H$ ,  $A$ ,  $F$ ,  $\mu$ , and  $f$  in terms of the independent variables  $V$  and  $T$ .

In terms of the independent variables  $V$  and  $T$ , Equation (16.23) becomes

$$C_V - T \frac{(\partial p / \partial T)_V^2}{(\partial p / \partial V)_T} \quad (17.15)$$

The relation

$$dC_V = T \left( \frac{\partial^2 p}{\partial T^2} \right)_V dV \quad (T, n \text{ constant}) \quad (17.16)$$

can be integrated at constant temperature from  $V^*$  to  $V$ . The resulting definite integral can be shown to be a proper integral from Equation (14.7); and the limit  $V^*$  can be replaced by infinity. Then

$$C_V = nc_v^* - T \int_V^\infty \left( \frac{\partial^2 p}{\partial T^2} \right)_V dV \quad (17.17)$$

In a manner similar to that used in Section 16 we can express  $C_p$  as a function of  $(V, T, n)$ .

The Joule-Thomson and Joule coefficients become in terms of the independent variables  $V$  and  $T$

$$\mu_{J.T.} C_p = - \left[ V + T \frac{(\partial p / \partial T)_V}{(\partial p / \partial V)_T} \right] \quad (17.18)$$

$$\eta C_V = T^2 \left[ \frac{\partial(p/T)}{\partial T} \right]_V \quad (17.19)$$

All of the foregoing expressions are collected in Section 19.

(18) **General Equations for the Thermodynamic Properties of Pure Gases in Terms of  $p$  and  $T$ :** The following relations whose derivations are given in Section 16 may be considered general thermodynamic relations for pure gases. The only assumptions are those relating to the region of very low pressure.

$$E = \int_0^p \left[ V - T \left( \frac{\partial V}{\partial T} \right)_p \right] dp - pV + nh^0 \quad (18.1)$$

$$H = \int_0^p \left[ V - T \left( \frac{\partial V}{\partial T} \right)_p \right] dp + nh^0 \quad (18.2)$$

$$S = \int_0^p \left[ \frac{nR}{p} - \left( \frac{\partial V}{\partial T} \right)_p \right] dp - nR \ln p + ns^0 \quad (18.3)$$

$$A = \int_0^p \left[ V - \frac{nRT}{p} \right] dp + nRT \ln p - pV + n(h^0 - Ts^0) \quad (18.4)$$

$$F = \int_0^p \left[ V - \frac{nRT}{p} \right] dp + nRT \ln p + n(h^0 - Ts^0) \quad (18.5)$$

$$\mu = \int_0^p \left[ \frac{V}{n} - \frac{RT}{p} \right] dp + RT \ln p + h^0 - Ts^0 \quad (18.6)$$

$$RT \ln f = \int_0^p \left[ \frac{V}{n} - \frac{RT}{p} \right] dp + RT \ln p \quad (18.7)$$

$$C_p = nc_p^* - T \int_0^p \left( \frac{\partial^2 V}{\partial T^2} \right)_p dp \quad (18.8)$$

$$C_V = nc_v^* + nR + T \frac{(\partial V / \partial T)_p^2}{(\partial V / \partial p)_T} - T \int_0^p \left( \frac{\partial^2 V}{\partial T^2} \right)_p dp \quad (18.9)$$

$$C_p - C_V = -T \frac{(\partial V / \partial T)_p^2}{(\partial V / \partial p)_T} \quad (18.10)$$

$$\mu_{J.T.} C_p = T^2 \left[ \frac{\partial(V/T)}{\partial T} \right]_p \quad (18.11)$$

$$\eta C_V = - \frac{T(\partial V / \partial T)_p + p(\partial V / \partial p)_T}{(\partial V / \partial p)_T} \quad (18.12)$$

In the foregoing equations the definite integrals are to be evaluated at the temperature  $T$ . The integration constants are given by the expressions:

$$h^0 = h_0^0 + \int_{T_0}^T c_p^* dT \quad (18.13)$$

$$s^0 = s_0^0 + \int_{T_0}^T \frac{c_p^*}{T} dT \quad (18.14)$$

where the integrals are to be evaluated along the zero pressure curve and  $h_0^0$  and  $s_0^0$  are the molar heat content and entropy constants for the gas at  $T_0$ .

(19) **General Equations for the Thermodynamic Properties of Pure Gases in Terms of  $V$  and  $T$ :** The derivation of the following relations are given in Section 17.

$$E = \int_V^\infty \left[ p - T \left( \frac{\partial p}{\partial T} \right)_V \right] dV + ne^0 \quad (19.1)$$

$$H = \int_V^\infty \left[ p - T \left( \frac{\partial p}{\partial T} \right)_V \right] dV + pV + ne^0 \quad (19.2)$$

$$S = \int_V^\infty \left[ \frac{nR}{V} - \left( \frac{\partial p}{\partial T} \right)_V \right] dV + nR \ln \frac{V}{nRT} + ns^0 \quad (19.3)$$

$$A = \int_V^\infty \left[ p - \frac{nRT}{V} \right] dV - nRT \ln \frac{V}{nRT} + n(e^0 - Ts^0) \quad (19.4)$$

$$F = \int_V^\infty \left[ p - \frac{nRT}{A} \right] dV - nRT \ln \frac{V}{nRT} + pV + n(e^0 - Ts^0) \quad (19.5)$$

$$\mu = \int_V^\infty \left[ \left( \frac{\partial p}{\partial n} \right)_{VT} - \frac{RT}{V} \right] dV - RT \ln \frac{V}{nRT} + RT + e^0 - Ts^0 \quad (19.6)$$

$$RT \ln f = \int_V^\infty \left[ \left( \frac{\partial p}{\partial n} \right)_{VT} - \frac{RT}{V} \right] dV - RT \ln \frac{V}{nRT} \quad (19.7)$$

$$C_p = nc_p^* - nR - T \frac{(\partial p / \partial T)_V^2}{(\partial p / \partial V)_T} - T \int_V^\infty \left( \frac{\partial^2 p}{\partial T^2} \right)_V dV \quad (19.8)$$

$$C_V = nc_v^* - T \int_V^\infty \left( \frac{\partial^2 p}{\partial T^2} \right)_T dV \quad (19.9)$$

$$C_p - C_V = -T \frac{(\partial p / \partial T)_V^2}{(\partial p / \partial V)_T} \quad (19.10)$$

$$\mu_{J.T.} C_p = - \frac{T(\partial p / \partial T)_V + V(\partial p / \partial V)_T}{(\partial p / \partial V)_T} \quad (19.11)$$

$$\eta C_V = T^2 \left[ \frac{\partial(p/T)}{\partial T} \right]_V \quad (19.12)$$

In these relations the definite integrals are to be evaluated at the temperature  $T$ , and

$$e^0 = e_0^0 + \int_{T_0}^T c_v^* dT; \quad e_0^0 = h_0^0 - RT_0 \quad (19.13)$$

$$s^0 = s_0^0 + \int_{T_0}^T \frac{c_v^*}{T} dT + R \ln \frac{T}{T_0} \quad (19.14)$$

The temperature integral is to be evaluated along the zero pressure curve.

(20) **Integrated Equations for the Thermodynamic Properties of Pure Gases in Terms of  $p$  and  $T$ :** The general relations of Section 18 can be expressed in terms of the virial parameters of the equation of state (6.3) explicit in the volume:

$$V = \frac{nRT}{RT} + \frac{n\beta}{RT} + \frac{n\gamma}{(RT)^2} p + \frac{n\delta}{(RT)^3} p^2$$

The derivatives of the virial parameters are given in Section 10. The values of the equation of state constants determined for this form of equation of state should be used in the following relations. The order of magnitude of the error introduced by using the constants for the equation explicit in the pressure, as

listed in Table II, can be estimated by a comparison of Equations (6.2) and (6.3). More accurate values can be obtained by replacing  $\gamma$  and  $\delta$  in the following expressions by the coefficients of  $p$  and  $p^2$  of Equation (6.2). For better results the equations of Section 21 must be used, the thermodynamic quantities being computed at the temperature in question for a series of densities and the corresponding pressure computed from the equation of state explicit in the pressure.

$$E = \left( \beta - T \frac{d\beta}{dT} \right) \frac{np}{RT} + \left( \gamma - T \frac{d\gamma}{dT} \right) \frac{np^2}{2(RT)^2} + \left( \delta - T \frac{d\delta}{dT} \right) \frac{np^3}{3(RT)^3} - nRT + nh^0 \quad (20.1)$$

$$H = \left( 2\beta - T \frac{d\beta}{dT} \right) \frac{np}{RT} + \left( 3\gamma - T \frac{d\gamma}{dT} \right) \frac{np^2}{2(RT)^2} + \left( 4\delta - T \frac{d\delta}{dT} \right) \frac{np^3}{3(RT)^3} + nh^0 \quad (20.2)$$

$$S = -nR \ln p + \left( \frac{\beta}{T} - \frac{d\beta}{dT} \right) \frac{np}{RT} + \left( 2 \frac{\gamma}{T} - \frac{d\gamma}{dT} \right) \frac{np^2}{2(RT)^2} + \left( 3 \frac{\delta}{T} - \frac{d\delta}{dT} \right) \frac{np^3}{3(RT)^3} + ns^0 \quad (20.3)$$

$$A = nRT \ln p - \gamma \frac{np^2}{2(RT)^2} - 2\delta \frac{np^3}{3(RT)^3} - nRT + nh^0 - nTs^0 \quad (20.4)$$

$$F = nRT \ln p + \beta \frac{np}{RT} + \gamma \frac{np^2}{2(RT)^2} + \delta \frac{np^3}{3(RT)^3} + nh^0 - nTs^0 \quad (20.5)$$

$$\mu = RT \ln p + \beta \frac{p}{RT} + \gamma \frac{p^2}{2(RT)^2} + \delta \frac{p^3}{3(RT)^3} + h^0 - Ts^0 \quad (20.6)$$

$$RT \ln f = RT \ln p + \beta \frac{p}{RT} + \gamma \frac{p^2}{2(RT)^2} + \delta \frac{p^3}{3(RT)^3} \quad (20.7)$$

$$C_p = nc_p^* - \left( 2 \frac{\beta}{T} - 2 \frac{d\beta}{dT} + T \frac{d^2\beta}{dT^2} \right) \frac{np}{RT} - \left( \frac{6\gamma}{T} - \frac{4d\gamma}{dT} + T \frac{d^2\gamma}{dT^2} \right) \frac{np^2}{2(RT)^2} - \left( 12 \frac{\delta}{T} - 6 \frac{d\delta}{dT} + T \frac{d^2\delta}{dT^2} \right) \frac{np^3}{3(RT)^3} \quad (20.8)$$

$$C_V = nc_v^* + nR$$

$$\begin{aligned} nT \left[ R - \left( \frac{\beta}{T} - \frac{d\beta}{dT} \right) \frac{p}{RT} - \left( 2 \frac{\gamma}{T} - \frac{d\gamma}{dT} \right) \frac{p^2}{(RT)^2} \right. \\ \left. - \left( 3 \frac{\delta}{T} - \frac{d\delta}{dT} \right) \frac{p^3}{(RT)^3} \right]^2 \\ RT - \gamma \frac{p^2}{(RT)^2} - 2\delta \frac{p^3}{(RT)^3} \\ - \left( 2 \frac{\beta}{T} - 2 \frac{d\beta}{dT} + T \frac{d^2\beta}{dT^2} \right) \frac{np}{RT} \\ - \left( 6 \frac{\gamma}{T} - 4 \frac{d\gamma}{dT} + T \frac{d^2\gamma}{dT^2} \right) \frac{np^2}{2(RT)^2} \\ - \left( 12 \frac{\delta}{T} - 6 \frac{d\delta}{dT} + T \frac{d^2\delta}{dT^2} \right) \frac{np^3}{3(RT)^3} \quad (20.9) \end{aligned}$$

$$\begin{aligned} nT \left[ R - \left( \frac{\beta}{T} - \frac{d\beta}{dT} \right) \frac{p}{RT} - \left( 2 \frac{\gamma}{T} - \frac{d\gamma}{dT} \right) \frac{p^2}{(RT)^2} \right. \\ \left. - \left( 3 \frac{\delta}{T} - \frac{d\delta}{dT} \right) \frac{p^3}{(RT)^3} \right]^2 \\ C_p - C_V = \frac{RT - \gamma \frac{p^2}{(RT)^2} - 2\delta \frac{p^3}{(RT)^3}}{RT - \gamma \frac{p^2}{(RT)^2} - 2\delta \frac{p^3}{(RT)^3}} \quad (20.10) \end{aligned}$$

$$\begin{aligned} \text{r.t. } C_p = - \left( 2\beta - T \frac{d\beta}{dT} \right) \frac{n}{RT} - \left( 3\gamma - T \frac{d\gamma}{dT} \right) \frac{np}{(RT)^2} \\ - \left( 4\delta - T \frac{d\delta}{dT} \right) \frac{np^2}{(RT)^3} \quad (20.11) \end{aligned}$$

$$\begin{aligned} - \left( \beta - T \frac{d\beta}{dT} \right) \frac{p^2}{RT} - \left( \gamma - T \frac{d\gamma}{dT} \right) \frac{p^3}{(RT)^2} \\ - \left( \delta - T \frac{d\delta}{dT} \right) \frac{p^4}{(RT)^3} \\ \eta C_V = \frac{RT - \gamma \frac{p^2}{(RT)^2} - 2\delta \frac{p^3}{(RT)^3}}{RT - \gamma \frac{p^2}{(RT)^2} - 2\delta \frac{p^3}{(RT)^3}} \quad (20.12) \end{aligned}$$

(21) **Integrated Equations for the Thermodynamic Properties of Pure Gases in Terms of  $V$  and  $T$ :** The general thermodynamic relations of Section 19 can be expressed in terms of the virial parameters of the equation of state (6.1):

$$p = \frac{nRT}{V} + \frac{n^2\beta}{V^2} + \frac{n^3\gamma}{V^3} + \frac{n^4\delta}{V^4}$$

The derivatives of the parameters expressed as function of temperature and the equation of state constants are given in Section 10.

$$E = \left( \beta - T \frac{d\beta}{dT} \right) \frac{n^2}{V} + \left( \gamma - T \frac{d\gamma}{dT} \right) \frac{n^3}{2V^2} + \left( \delta - T \frac{d\delta}{dT} \right) \frac{n^4}{3V^3} + ne^0 \quad (21.1)$$

$$H = \left( 2\beta - T \frac{d\beta}{dT} \right) \frac{n^2}{V} + \left( 3\gamma - T \frac{d\gamma}{dT} \right) \frac{n^3}{2V^2} + \left( 4\delta - T \frac{d\delta}{dT} \right) \frac{n^4}{3V^3} + nRT + ne^0 \quad (21.2)$$

$$S = nR \ln \frac{V}{nRT} - \frac{d\beta}{dT} \frac{n^2}{V} - \frac{d\gamma}{dT} \frac{n^3}{2V^2} - \frac{d\delta}{dT} \frac{n^4}{3V^3} + ns^0 \quad (21.3)$$

$$A = -nRT \ln \frac{V}{nRT} + \beta \frac{n^2}{V} + \gamma \frac{n^3}{2V^2} + \delta \frac{n^4}{3V^3} + ne^0 - nTs^0 \quad (21.4)$$

$$F = -nRT \ln \frac{V}{nRT} + 2\beta \frac{n^2}{V} + 3\gamma \frac{n^3}{2V^2} + 4\delta \frac{n^4}{3V^3} + nRT + ne^0 - nTs^0 \quad (21.5)$$

$$\mu = -RT \ln \frac{V}{nRT} + 2\beta \frac{n}{V} + 3\gamma \frac{n^2}{2V^2} + 4\delta \frac{n^3}{3V^3} + RT + e^0 - Ts^0 \quad (21.6)$$

$$RT \ln f = -RT \ln \frac{V}{nRT} + 2\beta \frac{n}{V} + 3\gamma \frac{n^2}{2V^2} + 4\delta \frac{n^3}{3V^3} \quad (21.7)$$

$$C_p = nc_p^* - nR + \frac{nT \left[ R + \frac{d\beta}{dT} \frac{n}{V} + \frac{d\gamma}{dT} \frac{n^2}{V^2} + \frac{d\delta}{dT} \frac{n^3}{V^3} \right]^2}{RT + 2\beta \frac{n}{V} + 3\gamma \frac{n^2}{V^2} + 4\delta \frac{n^3}{V^3}} - T \frac{d^2\beta}{dT^2} \frac{n^2}{V} - T \frac{d^2\gamma}{dT^2} \frac{n^3}{2V^2} - T \frac{d^2\delta}{dT^2} \frac{n^4}{3V^3} \quad (21.8)$$

$$C_v = nc_v^* - T \frac{d^2\beta}{dT^2} \frac{n^2}{V} - T \frac{d^2\gamma}{dT^2} \frac{n^3}{2V^2} - T \frac{d^2\delta}{dT^2} \frac{n^4}{3V^3} \quad (21.9)$$

$$C_p - C_v = \frac{nT \left[ R + \frac{d\beta}{dT} \frac{n}{V} + \frac{d\gamma}{dT} \frac{n^2}{V^2} + \frac{d\delta}{dT} \frac{n^3}{V^3} \right]^2}{RT + 2\beta \frac{n}{V} + 3\gamma \frac{n^2}{V^2} + 4\delta \frac{n^3}{V^3}} \quad (21.10)$$

$$\mu_{J.T.} C_p = \frac{-\left(2\beta - T \frac{d\beta}{dT}\right)n - \left(3\gamma - T \frac{d\gamma}{dT}\right)\frac{n^2}{V} - \left(4\delta - T \frac{d\delta}{dT}\right)\frac{n^3}{V^2}}{RT + 2\beta \frac{n}{V} + 3\gamma \frac{n^2}{V^2} + 4\delta \frac{n^3}{V^3}} \quad (21.11)$$

$$\eta C_V = -\left(\beta - T \frac{d\beta}{dT}\right)\frac{n^2}{V^2} - \left(\gamma - T \frac{d\gamma}{dT}\right)\frac{n^3}{V^3} - \left(\delta - T \frac{d\delta}{dT}\right)\frac{n^4}{V^4} \quad (21.12)$$

(22) **Integrated Approximate Equations for the Thermodynamic Properties of Pure Gases in Terms of  $p$  and  $T$ :** The relations given in this section are a sufficiently good approximation for many purposes. They are derived from the equations of Section 20 by dropping terms of higher order in the pressure and are expressed in terms of the equation of state constants rather than the virial parameters. The values of the constants to be employed are those listed in Table II determined for the equation explicit in the pressure. For the most part the expression given here may be derived from the general relations of Section 18 and the Equation (6.5):

$$\frac{nRT}{p} + \frac{n\beta}{RT}$$

$$E = -\left[\frac{A_0}{RT} + \frac{3c}{T^3}\right]np - nRT + nh^0 \quad (22.1)$$

$$H = \left[B_0 - \frac{2A_0}{RT} - \frac{4c}{T^3}\right]np + nh^0 \quad (22.2)$$

$$S = -nR \ln p - \left[\frac{\ddot{A}_0}{RT^2} + \frac{\ddot{c}}{T^4}\right]np + \quad (22.3)$$

$$A = nRT \ln p - nRT + nh^0 - nTs^0 \quad (22.4)$$

$$F = nRT \ln p + \left[B_0 - \frac{A_0}{RT} - \frac{c}{T^3}\right]np + nh^0 - nTs^0 \quad (22.5)$$

$$\mu = RT \ln p + \left[B_0 - \frac{A_0}{RT} - \frac{c}{T^3}\right]p + h^0 - Ts^0 \quad (22.6)$$

$$RT \ln f = RT \ln p + \left[B_0 - \frac{A_0}{RT} - \frac{c}{T^3}\right]p \quad (22.7)$$

$$nc_p^* + \left[\frac{2A_0}{RT^2} + \frac{12c}{T^4}\right]np \quad (22.8)$$

$$C_V = nc_v^* + \frac{6c}{T^4}np \quad (22.9)$$

$$C_p - C_V = nR + \left[\frac{2A_0}{RT^2} + \frac{6c}{T^4}\right]np \quad (22.10)$$



$$\mu_{J.T.}C_p = - \left[ B_0 - \frac{2A_0}{RT} - \frac{4c}{T^3} \right] n + \left[ \frac{2B_0b}{RT} - \frac{3A_0a}{(RT)^2} + \frac{5B_0c}{RT^4} \right] np \quad (22.11)$$

$$\eta C_V = \left[ \frac{A_0}{(RT)^2} + \frac{3c}{RT^4} \right] p^2 \quad (22.12)$$

(23) **General Equations for the Thermodynamic Properties of Pure Gases in Terms of  $p_r$  and  $T_r$ , and the Compressibility Factor:** The thermodynamic properties of gases are derived in many engineering calculations from plots of the compressibility factor  $Z (= pV/nRT)$  against the reduced pressure  $p_r$  for a series of reduced isotherms  $T_r$ . The general thermodynamic equations of Section 18 can be expressed in these variables. The integrals and partial derivatives are evaluated graphically from the generalized  $Z$  chart.

$$\frac{E}{nRT_c} = -T_r^2 \int_0^{p_r} \left( \frac{\partial Z}{\partial T_r} \right)_{p_r} d \ln p_r - T_r Z + h_r^0 \quad (23.1)$$

$$\frac{H}{nRT_c} = -T_r^2 \int_0^{p_r} \left( \frac{\partial Z}{\partial T_r} \right)_{p_r} d \ln p_r + h_r^0 \quad (23.2)$$

$$\frac{S}{nR} = \int_0^{p_r} \left[ 1 - Z - T_r \left( \frac{\partial Z}{\partial T_r} \right)_{p_r} \right] d \ln p_r - \ln p_r + s_r^0 \quad (23.3)$$

$$\frac{A}{nRT_c} = T_r \int_0^{p_r} (Z - 1) d \ln p_r + T_r \ln p_r \quad (23.4)$$

$$\frac{F}{nRT_c} = T_r \int_0^{p_r} (Z - 1) d \ln p_r + T_r \ln p_r + h_r^0 - T_r s_r^0 \quad (23.5)$$

$$\frac{\mu}{RT_c} = T_r \int_0^{p_r} (Z - 1) d \ln p_r + T_r \ln p_r + h_r^0 - T_r s_r^0 \quad (23.6)$$

$$\ln \frac{f}{p} = \int_0^{p_r} (Z - 1) d \ln p_r \quad (23.7)$$

$$\frac{C_p}{nR} = \frac{c_p^*}{R} - \int_0^{p_r} \left[ 2T_r \left( \frac{\partial Z}{\partial T_r} \right)_{p_r} + T_r^2 \left( \frac{\partial^2 Z}{\partial T_r^2} \right)_{p_r} \right] d \ln p_r \quad (23.8)$$

$$\frac{C_V}{nR} = \frac{c_v^*}{R} + 1 - \int_0^{p_r} \left[ 2T_r \left( \frac{\partial Z}{\partial T_r} \right)_{p_r} + T_r^2 \left( \frac{\partial^2 Z}{\partial T_r^2} \right)_{p_r} \right] d \ln p_r$$

$$\frac{[Z + T_r(\partial Z/\partial T_r)_{p_r}]^2}{Z - p_r(\partial Z/\partial p_r)_{T_r}} \quad (23.9)$$

$$\frac{C_p}{nR} - \frac{C_V}{nR} = \frac{[Z + T_r(\partial Z/\partial T_r)_{p_r}]^2}{Z - p_r(\partial Z/\partial p_r)_{T_r}} \quad (23.10)$$

$$nRT_c^{\mu_{J.T.}C_p} \frac{T_r^2}{p_r} \left( \frac{\partial Z}{\partial T_r} \right)_{p_r} \quad (23.11)$$

$$\frac{1}{p_c} \eta C_V = \left[ \frac{T_r(\partial Z/\partial T_r)_{p_r} + p_r(\partial Z/\partial p_r)_{T_r}}{Z - p_r(\partial Z/\partial p_r)_{T_r}} \right] p_r \quad (23.12)$$

In the foregoing equations the definite integrals are to be evaluated at the reduced temperature  $T_r$ . The integration constants are given by the expressions:

$$h_r^0 = \frac{h_0^0}{RT_c} + \frac{1}{R} \int_{T_0}^{T_r} c_p^* dT_r \quad (23.13)$$

$$s_r^0 = \frac{s_0^0}{R} + \frac{1}{R} \int_{T_0}^{T_r} \frac{c_p^*}{T_r} dT_r - \ln p_c \quad (23.14)$$

Here  $h_0^0$  and  $s_0^0$  are the heat content and entropy constants of the substance at the standard temperature  $T_0$  as in the earlier equations; and  $c_p^*$  is to be given as a function of the reduced temperature  $T_r$ .

#### THERMODYNAMIC TREATMENT OF GAS MIXTURES

(24) **General Considerations:** In order to give a general thermodynamic treatment of gas mixtures including mixtures in which chemical reaction may occur we need one assumption that permits expressing the chemical potential of a gas in a mixture in terms of the chemical potential of the pure gas. The resulting equations contain, in general, definite integrals that can be evaluated from an equation of state of gas mixtures or, in some cases, from an equation of state for pure gases, or an equivalent graphical method. Three proposals as a starting point for gas mixtures have received considerable attention:

1. *The General Limit Method for Gas Mixtures.* An equation of state for gas mixtures is required for evaluation of the definite integrals appearing in the general relations.

2. *The Lewis and Randall Rule.*<sup>1</sup> The properties of gas mixtures are expressed in terms of the properties of pure gases. An equation of state for pure gases explicit in the volume or an equivalent graphical method is needed.

3. *The Gibbs-Dalton Law.*<sup>2</sup> The properties of gas mixtures are given in terms of the properties of pure gases. An equation of state for pure gases explicit in the pressure or an equivalent graphical method is required.

The general relations given by the first procedure may be considered exact, approximations being introduced by use of an equation of state of gas mixtures. The general relations of the other two procedures are approximate.

<sup>1</sup> G. N. Lewis and M. Randall, *Thermodynamics* (New York: McGraw-Hill Book Co., Inc., 1923), pp. 225-7.

<sup>2</sup> J. W. Gibbs, *Scientific Papers*, Vol. I (New York: Longmans, Green and Company, 1906), pp. 155-8; L. J. Gillespie, *Phys. Rev.*, **36**, 121 (1930).

(25) **Notation:** Let  $p$ ,  $V$ ,  $T$  be the total pressure, total volume, and Kelvin temperature; and  $E$ ,  $S$ ,  $H$ ,  $A$ ,  $F$ ,  $C_V$ , and  $C_p$  be the total energy, entropy, heat content, work content, free energy, and constant-volume and constant-pressure heat capacities, respectively, of  $(\sum_i n_i)$  moles of a gas mixture consisting of  $n_1$ ,  $n_2$ ,  $\dots$  moles of the gases 1, 2,  $\dots$ . Let  $\mu_i$  be the chemical potential of gas  $i$  in a mixture.

Let  $C = (\sum_i n_i/V)$  be the concentration of the mixture; and let  $C_i = n_i/V$ ,  $x_i = n_i/(\sum_i n_i)$ , and  $f_i$  be, respectively, the concentration, mole fraction, and fugacity of gas  $i$  in the mixture.

Lower case letters used for an extensive quantity denote the value for one mole.

If it is necessary to distinguish between a pure gas and the same gas in a mixture, the subscript  $k$  will denote the value of a quantity for the pure gas and  $i$  that for the gas in the mixture.

The subscript  $e$  denotes the value of a thermodynamic quantity for a pure gas having the same total volume, temperature, and chemical potential as in a gas mixture. Under these conditions the pure gas would evidently be in thermodynamic equilibrium with the mixture through a membrane permeable to that gas alone; and, since the volume is specified, the values of all extensive as well as intensive properties of the gas would be fixed. Such quantities will be called equilibrium quantities,<sup>1</sup> e.g., equilibrium pressure,  $p_e$ .

The subscript  $c$  denotes the value of a thermodynamic quantity for a pure gas having the same total volume, temperature, and number of moles as in a mixture. The concentration (moles per liter) of the pure gas is the same as its concentration in the mixture. Thus  $p_c$  is the pressure exerted by a gas that has been separated from a mixture and has the total volume and temperature of the mixture.

The subscript  $P$  denotes the value of a thermodynamic quantity for a pure gas having the same total pressure, temperature, and number of moles as in a mixture. Thus  $V_P$  is the volume of a pure gas that has been separated from a mixture and is at the total pressure and temperature of the mixture.

Let  $\nu_i$  be the stoichiometric coefficient of a constituent  $i$  in the equation representing a chemical reaction, being a negative number for a reactant and positive for a product. The exact mass action law is

$$(\sum_i \nu_i \mu_i) = 0 \quad (25.1)$$

The mass action "constants" or functions in terms of partial pressures,  $K_p$ , and concentrations,  $K_C$ , are defined through the relations

$$\ln K_p = (\sum_i \nu_i \ln p x_i) \quad (25.2)$$

$$\ln K_C = \left( \sum_i \nu_i \ln \frac{n_i}{V} \right) \quad (25.3)$$

<sup>1</sup> L. J. Gillespie, *J. Am. Chem. Soc.*, **47**, 305 (1925).

In the discussion of equilibrium between condensed and gaseous solutions, we shall let  $y_i$  be the mole fraction of the  $i$ -th constituent of the condensed phase, and  $p_{0i}$  the vapor pressure of the pure constituent at the temperature  $T$  and under its own vapor pressure.

The term partial pressure of a gas  $i$  in a mixture is reserved for the product  $px_i$  where  $p$  is the total pressure of the mixture.

Thermodynamic relations among certain of the variables are:

$$E = TS - pV + (\sum_i \mu_i n_i) \quad (25.4)$$

$$H = E + pV = TS + (\sum_i \mu_i n_i) \quad (25.5)$$

$$A = E - TS = -pV + (\sum_i \mu_i n_i) \quad (25.6)$$

$$F = H - TS = (\sum_i \mu_i n_i) \quad (25.7)$$

$$C_V = (\partial E / \partial T)_{V, n} \quad (25.8)$$

$$C_p = (\partial H / \partial T)_{p, n} \quad (25.9)$$

where the subscript  $n$  denotes constant composition as well as constant total number of moles if for a gas mixture.

(26) **General Limit Method Assumption for Gas Mixtures:** We shall make the following assumption<sup>1</sup> as a starting point for the thermodynamic treatment of gas mixtures:

At all temperatures the ratio of the equilibrium pressure of each gas in a mixture to the product of the mole fraction of that gas in the mixture into the total pressure of the mixture can be represented in the region of low pressures by the expression:

$$\frac{p_{ek}}{px_i} = 1 + D_i(T, x_1, x_2, \dots)p + O(p^2) \quad (i \equiv k = 1, 2, \dots) \quad (26.1)$$

where  $D_i$  depends only on the temperature and composition of the mixture, and  $D_i$  and its derivatives with respect to  $T$ ,  $n_1$ ,  $n_2$ ,  $\dots$  are bounded.

(27) **Relations for Gas Mixtures in the Region of Low Pressure:** Consider a system of  $(\sum_i n_i)$  moles of a gas mixture and  $k$  systems each containing  $n_{ek}$  moles of one of the constituent gases. In all variations let:

$$\left. \begin{aligned} T \text{ (each pure gas)} &= T \text{ (mixture)} \\ V \text{ (each pure gas)} &= V \text{ (mixture)} \\ \mu_k &= \mu_i \quad (i \equiv k = 1, 2, \dots) \end{aligned} \right\} \quad (C)$$

Each pure gas would be in equilibrium with the mixture if separated from it by a membrane permeable to that gas alone. Hence the properties of the pure gases may be called equilibrium properties of the mixture.

<sup>1</sup> J. A. Beattie, *Phys. Rev.*, 36, 132 (1930).

Subject to the condition (C) the general limit method, Equation (26.1), gives the following results for the region of low pressure:

$$1. (\Sigma_k p_{ek}) = p(1 + D_m p), \quad (27.1)$$

where  $D_m$  is a function of temperature and composition ( $= \Sigma_i x_i D_i$ ).

$$\left. \begin{aligned} 2. \quad n_{ek} \quad \frac{n_i}{V} (1 + 2D_m p) \quad (i \equiv k = 1, 2, \dots) \\ C_{ek} = C_i (1 + 2D_m p) \\ = C x_i (1 + 2D_m p) \\ n_{ek} = n_i (1 + 2D_m p) \end{aligned} \right\} \quad (27.2)$$

$$3. (\Sigma_k S_{ek}) = S(1 + 2D_m p) \quad (27.3)$$

$$\left. \begin{aligned} 4. \quad pV &= (\Sigma_i n_i)RT + \frac{(\Sigma_i n_i)\beta_m}{RT} p \\ pV &= (\Sigma_i n_i)RT + \frac{(\Sigma_i n_i)^2 \beta_m}{V} \end{aligned} \right\} \quad (27.4)$$

where  $\beta_m$  is a bounded function of temperature and the composition of the gas mixture.

$$\left. \begin{aligned} 5. \quad (\Sigma_k E_{ek}) &= E(1 + 2D_m p) + (D_m p V)p \\ (\Sigma_k H_{ek}) &= H(1 + 2D_m p) \\ (\Sigma A_{ek}) &= A(1 + 2D_m p) + (D_m p V)p \\ (\Sigma F_{ek}) &= F(1 + 2D_m p) \\ (\Sigma_k C_{Vek}) &= C_V(1 + 2D_m p) + \alpha p \\ (\Sigma_k C_{pek}) &= C_p(1 + 2D_m p) + \alpha' p \end{aligned} \right\} \quad (27.5)$$

where  $\alpha$  and  $\alpha'$  are bounded functions of temperature and the composition of the gas mixture.

To prove these relations we take as independent variables  $T, \mu_1, \mu_2, \dots$  for the gas mixture and  $T, \mu_k$  for each pure gas. Equation (27.1) follows from Equation (26.1), which may be written for the region of low pressure

$$p_{ek} = p x_i (1 + D_i p) \quad (27.6)$$

The thermodynamic relation having  $T, \mu_1, \mu_2, \dots$  as independent variables is Gibbs' Equation (97).<sup>1</sup> Written for the gas mixture this equation is

$$dp = (S/V)dT + [\Sigma_i (n_i/V)d\mu_i] \quad (27.7)$$

and for each pure gas

$$dp_{ek} = (S_{ek}/V)dT + (n_{ek}/V)d\mu_k \quad (k = 1, 2, \dots) \quad (27.8)$$

<sup>1</sup> J. W. Gibbs, *Scientific Papers*, Vol. I (New York: Longmans, Green and Company, 1906), p. 88.

Thus

$$\left(\frac{\partial p}{\partial \mu_i}\right)_{T\mu} = \frac{n_i}{V} \equiv C_i \quad \left(\frac{\partial p}{\partial T}\right)_\mu = \frac{S}{V} \quad (i = 1, 2, \quad (27.9)$$

$$\left(\frac{\partial p_{ek}}{\partial \mu_k}\right)_T = \frac{n_{ek}}{V} \equiv C_{ek} \quad \left(\frac{\partial p_{ek}}{\partial T}\right)_{\mu_k} = \frac{S_{ek}}{V} \quad (k = 1, 2, \dots) \quad (27.10)$$

The subscript  $\mu$  in Equation (27.9) denotes that all of the  $\mu$ 's are constant unless the differentiation is with respect to one of the  $\mu$ 's, in which case all of the other  $\mu$ 's are constant.

Differentiating Equation (27.1) first with respect to one of the  $\mu$ 's with  $T$  and all of the other  $\mu$ 's constant, and then with respect to  $T$  with all of the  $\mu$ 's constant, we find for the region of low pressure

$$\left(\frac{\partial p_{ek}}{\partial \mu_k}\right)_T = \left(\frac{\partial p}{\partial \mu_i}\right)_{T\mu} (1 + 2D_m p) \quad (i \equiv k = 1, 2, \dots) \quad (27.11)$$

$$\Sigma_k \left(\frac{\partial p_{ek}}{\partial T}\right)_{\mu_k} = \left(\frac{\partial p}{\partial T}\right)_\mu (1 + 2D_m p) \quad (27.12)$$

Use of Equations (27.9) and (27.10) gives the first of Equations (27.2) and Equation (27.3). The remainder of the Equations (27.2) follow from the definitions given in Section 25 and the second of the conditions (C).

Division of Equation (27.6) by the first of Equations (27.2) gives for the region of low pressure

$$\frac{p_{ek}V}{n_{ek}} = \frac{pV}{(\Sigma_i n_i)} [1 + (D_i - 2D_m)p] \quad (27.13)$$

Now the left-hand side of this equation refers to the pure gas  $k$  existing by itself, and hence Equation (14.6) applies. Thus in the region of low pressure

$$\begin{aligned} \frac{pV}{(\Sigma_i n_i)} [1 + (D_i - 2D_m)p] &= RT + \frac{\beta p_{ek}}{RT} \\ &= RT + \frac{\nu}{RT} p x_i (1 + D_i p) \end{aligned} \quad (27.14)$$

where  $T$  is thermodynamic absolute temperature. This can be written in the form of the first of Equations (27.4) where  $\beta_m$  is a function of  $T$ ,  $x_1$ ,  $x_2$ ,  $\dots$ ; the second Equation (27.4) follows from the first to terms of the order of the density.

The relation

$$E = TS - pV + (\Sigma_i \mu_i n_i) \quad (27.15)$$

holds for the gas mixture, and

$$E_{ek} = TS_{ek} - p_{ek}V + \mu_k n_{ek} \quad (k = 1, 2, \dots) \quad (27.16)$$

for each of the pure gases. The first of Equations (27.5) follows from these relations, the conditions (C), and Equations (27.1), (27.2), and (27.3). The remaining relations (27.5) come from the definitions of  $H$ ,  $A$ ,  $F$ ,  $C_p$ , and  $C_V$ , Equations (25.5) to (25.9), and (14.7).

(28) **Relations for Gas Mixtures in the Region of Very Low Pressures:** As the pressure  $p$  on a pure gas becomes very small at constant temperature, the relations of Sections 14 and 18 show that the functions  $pV$ ,  $E$ ,  $H$ ,  $C_p$ , and  $C_V$  approach constant values while  $S$ ,  $A$ , and  $F$  increase or decrease in the same manner as  $\pm \ln p$ . The same must be true of a gas mixture of constant composition. But

$$\lim_{p \rightarrow 0} p \ln p = 0 \quad (28.1)$$

Hence we have for the region of very low pressures the following relations which may be derived by dropping the terms of the order of  $p$  from the relations of Section 27:

1. Equilibrium relationships:

$$\left. \begin{aligned} \left( \frac{p_{ek}}{px_i} \right)^* &= 1 & \left( \frac{C_{ek}}{C_i} \right)^* &= 1 & \left( \frac{C_{ek}}{Cx_i} \right)^* &= 1 \\ \left( \frac{n_{ek}}{n_i} \right)^* &= 1 & (i \equiv k = 1, 2, \dots) && \end{aligned} \right\} \quad (28.2)$$

2. Additive relationships:

$$\left( \frac{\sum_k p_{ek}}{p} \right)^* = 1 \quad \left( \frac{\sum_k C_{ek}}{C} \right)^* = 1 \quad (28.3)$$

$$S^* = (\sum_k S_{ek}) \quad (28.4)$$

$$\left. \begin{aligned} E^* &= (\sum_k E_k^*) & H^* &= (\sum_k H_k^*) & F^* &= (\sum_k F_{ek}^*) \\ A^* &= (\sum_k A_{ek}^*) & C_V^* &= (\sum_k C_{V_k}^*) & C_p^* &= (\sum_k C_{p_k}^*) \end{aligned} \right\} \quad (28.5)$$

3. The equation of state (independent of the conditions [C]):

$$(pV)^* = (\sum_i n_i)RT$$

The designation  $e$  can be omitted in the relations for  $E$ ,  $H$ ,  $C_V$ , and  $C_p$ , since these quantities are essentially constant in the region of very low pressure at constant temperature and mole numbers.

(29) **Derivations for the Independent Variables  $p$  and  $T$ :** Corresponding to Equations (16.3) and (16.5) for the heat content and entropy of a pure gas,

we have for  $(\Sigma_i n_i)$  moles of a gas mixture of constant composition

$$H(p, T) - H(p_0, T_0) = \int_{T_0}^{p^*} \left[ V - T \left( \frac{\partial V}{\partial T} \right)_{pn} \right] dp + \int_{p^*}^T C_p^* dT + \int_T^{p^*} \left[ V - T \left( \frac{\partial V}{\partial T} \right)_{pn} \right] dp \quad (29.1)$$

$$S(p, T) - S(p_0, T_0) = \int_{T_0}^{p^*} \left[ \frac{(\Sigma_i n_i)R}{p} - \left( \frac{\partial V}{\partial T} \right)_{pn} \right] dp + \int_{p^*}^T \frac{C_p^*}{T} dT + \int_T^{p^*} \left[ \frac{(\Sigma_i n_i)R}{p} - \left( \frac{\partial V}{\partial T} \right)_{pn} \right] dp - (\Sigma_i n_i)R \ln \frac{p}{p_0} \quad (29.2)$$

where the subscript  $n$  denotes constant mole numbers and  $C_p^*$  is the heat capacity of  $(\Sigma_i n_i)$  moles of gas mixture at a very low pressure.

Now from Equations (28.5), (18.2), and (28.2)

$$H(p^*, T_0) = [\Sigma_k H_k(p^*, T_0)] = (\Sigma_k n_{ek} h_{0k}^0) = (\Sigma_i n_i h_{0i}^0) \quad (29.3)$$

where for convenience  $h_{0i}^0$  is written for  $h_{0k}^0$ , since this will lead to no confusion. And from Equations (28.4), (18.3), and (28.2)

$$S(p^*, T_0) = [\Sigma_k S_{ek}(p_{ek}^*, T_0)] = (\Sigma_k n_{ek} s_{0k}^0) - (\Sigma_k n_{ek} R \ln p_{ek}^*) = (\Sigma_i n_i s_{0i}^0) - (\Sigma_i n_i R \ln p^* x_i) \quad (29.4)$$

Also from Equations (28.5) and (28.2)

$$C_p^* = (\Sigma_k C_{pk}^*) = (\Sigma_k n_{ek} c_{pk}^*) = (\Sigma_i n_i c_{pi}^*) \quad (29.5)$$

Thus from Equations (29.1) and (29.3)

$$H(p_0, T_0) + \int_{T_0}^{p^*} \left[ V - T \left( \frac{\partial V}{\partial T} \right)_{pn} \right] dp = H(p^*, T_0) = (\Sigma_i n_i h_{0i}^0) \quad (29.6)$$

and from Equations (29.2) and (29.4)

$$S(p_0, T_0) + \int_{T_0}^{p^*} \left[ \frac{(\Sigma_i n_i)R}{p} - \left( \frac{\partial V}{\partial T} \right)_{pn} \right] dp + (\Sigma_i n_i)R \ln p_0 = S(p^*, T_0) + (\Sigma_i n_i)R \ln p^* = (\Sigma_i n_i s_{0i}^0) - (\Sigma_i n_i R \ln x_i) \quad (29.7)$$

We can now substitute from Equations (29.5), (29.6), and (29.7) into Equations (29.1) and (29.2). Then use of Equation (27.4) shows that we can replace the limit  $p^*$  by 0 (compare Equations [16.6] and [16.7]), and obtain

$$H(p, T) = \int_0^p \left[ V - T \left( \frac{\partial V}{\partial T} \right)_{pn} \right] dp + (\Sigma_i n_i h_i^0) \quad (29.8)$$

$$S(p, T) = \int_0^p \left[ \frac{(\Sigma_i n_i)R}{p} - \left( \frac{\partial V}{\partial T} \right)_{pn} \right] dp - (\Sigma_i n_i R \ln p x_i) + (\Sigma_i n_i s_i^0) \quad (29.9)$$

where  $h_i^0$  and  $s_i^0$  are given by Equations (18.13) and (18.14).



The other thermodynamic properties can now be written as was done for the pure gases. These are collected in Section 31.

(30) **Derivations for the Independent Variables  $V$  and  $T$ :** The relations for the energy and entropy of a gas mixture of constant composition corresponding to Equations (17.3) and (17.5) for pure gases are

$$E(V, T) - E(V_0, T_0) = \int_{T_0}^{V^*} \left[ T \left( \frac{\partial p}{\partial T} \right)_{V_n} - p \right] dV + \int_{V^*}^T C_{V^*} dT \\ + \int_T^{V^*} \left[ T \left( \frac{\partial p}{\partial T} \right)_{V_n} - p \right] dV, \quad (30.1)$$

$$S(V, T) - S(V_0, T_0) = \int_{T_0}^V \left[ \left( \frac{\partial p}{\partial T} \right)_{V_n} - \frac{(\Sigma_i n_i)R}{V} \right] dV + \int_{V^*}^T \frac{C_{V^*}}{T} dT \\ + \int_T^V \left[ \left( \frac{\partial p}{\partial T} \right)_{V_n} - \frac{(\Sigma_i n_i)R}{V} \right] dV + (\Sigma_i n_i)R \ln \frac{V}{V_0} \quad (30.2)$$

From Equations (28.5), (19.1), and (28.2) we find

$$E(V^*, T_0) = [\Sigma_k E_k(V^*, T_0)] = (\Sigma_k n_{ek} e_{0k}^0) = (\Sigma_i n_i e_{0i}^0) \quad (30.3)$$

and from Equations (28.4), (19.3), and (28.2)

$$S(V^*, T_0) = [\Sigma_k S_{ek}(V^*, T_0)] = (\Sigma_k n_{ek} s_{0k}^0) + \left( \Sigma_k n_{ek} R \ln \frac{V^*}{n_{ek} R T} \right) \\ = (\Sigma_i n_i s_{0i}^0) + \left( \Sigma_i n_i R \ln \frac{V^*}{n_i R T} \right) \quad (30.4)$$

Also from Equations (28.5) and (28.2)

$$C_{V^*} = (\Sigma_k C_{V_k}^*) = (\Sigma_k n_{ek} c_{v_k}^*) = (\Sigma_i n_i c_{v_i}^*) \quad (30.5)$$

From Equations (30.1) and (30.3) we find

$$E(V_0, T_0) + \int_{T_0}^{V^*} \left[ T \left( \frac{\partial p}{\partial T} \right)_{V_n} - p \right] dV = E(V^*, T_0) = (\Sigma_i n_i e_{0i}^0) \quad (30.6)$$

and from Equations (30.2) and (30.4)

$$S(V_0, T_0) + \int_{T_0}^{V^*} \left[ \left( \frac{\partial p}{\partial T} \right)_{V_n} - \frac{(\Sigma_i n_i)R}{V} \right] dV - (\Sigma_i n_i)R \ln V_0 \\ = S(V^*, T_0) - (\Sigma_i n_i)R \ln V^* = (\Sigma_i n_i s_{0i}^0) - (\Sigma_i n_i R \ln n_i R T) \quad (30.7)$$

Substitution from Equations (30.6) and (30.7) into (30.1) and (30.2), and replacement of  $V^*$  by infinity (compare Equations [17.13] and [17.14]) give

$$E = \int_V^\infty \left[ p - T \left( \frac{\partial p}{\partial T} \right)_{V_n} \right] dV + (\Sigma_i n_i e_i^0) \quad (30.8)$$

$$S = \int_V^\infty \left[ \frac{(\sum_i n_i)R}{V} - \left( \frac{\partial p}{\partial T} \right)_{V,n} \right] dV + \left( \sum_i n_i R \ln \frac{V}{n_i R T} \right) + (\sum_i n_i s_i^0) \quad (30.9)$$

Here  $e_i^0$  and  $s_i^0$  are given by Equations (19.13) and (19.14).

The other thermodynamic equations can now be written as before. They are collected in Section 32.

(31) **General Equations for the Thermodynamic Properties of Gas Mixtures in Terms of  $p$  and  $T$ :** The equations derived in Section 29 follow:

$$E = \int_0^p \left[ V - T \left( \frac{\partial V}{\partial T} \right)_{p,n} \right] dp - pV + [\sum_i n_i h_i^0] \quad (31.1)$$

$$H = \int_0^p \left[ V - T \left( \frac{\partial V}{\partial T} \right)_{p,n} \right] dp + (\sum_i n_i h_i^0) \quad (31.2)$$

$$S = \int_0^p \left[ \frac{(\sum_i n_i)R}{p} - \left( \frac{\partial V}{\partial T} \right)_{p,n} \right] dp - (\sum_i n_i R \ln p x_i) + (\sum_i n_i s_i^0) \quad (31.3)$$

$$A = \int_0^p \left[ V - \frac{(\sum_i n_i)RT}{p} \right] dp + (\sum_i n_i RT \ln p x_i) - pV + [\sum_i n_i (h_i^0 - T s_i^0)] \quad (31.4)$$

$$F = \int_0^p \left[ V - \frac{(\sum_i n_i)RT}{p} \right] dp + (\sum_i n_i RT \ln p x_i) + [\sum_i n_i (h_i^0 - T s_i^0)] \quad (31.5)$$

$$\mu_i = \int_0^p \left[ \left( \frac{\partial V}{\partial n_i} \right)_{p,T,n} - \frac{RT}{p} \right] dp + RT \ln p x_i + h_i^0 - T s_i^0 \quad (31.6)$$

$$RT \ln f_i = \int_0^p \left[ \left( \frac{\partial V}{\partial n_i} \right)_{p,T,n} - \frac{RT}{p} \right] dp + RT \ln p x_i \quad (31.7)$$

$$C_p = (\sum_i n_i c_{pi}^*) - T \int_0^p \left( \frac{\partial^2 V}{\partial T^2} \right)_{p,n} dp \quad (31.8)$$

$$C_V = (\sum_i n_i c_{vi}^*) + (\sum_i n_i)R + T \frac{(\partial V / \partial T)_{p,n}^2}{(\partial V / \partial p)_{T,n}} - T \int_0^p \left( \frac{\partial^2 V}{\partial T^2} \right)_{p,n} dp \quad (31.9)$$

$$C_p - C_V = \frac{(\partial V / \partial T)_{p,n}^2}{(\partial V / \partial p)_{T,n}} \quad (31.10)$$

$$\mu_{J.T.} C_p = T^2 \left[ \frac{\partial (V/T)}{\partial T} \right]_{p,n} \quad (31.11)$$

$$\eta C_V = - \frac{T(\partial V / \partial T)_{p,n} + p(\partial V / \partial p)_{T,n}}{(\partial V / \partial p)_{T,n}} \quad (31.12)$$

In the foregoing expressions the definite integrals are to be evaluated at the temperature  $T$  and at constant composition, and

$$h_i^0 = h_{0i}^0 + \int_{T_0}^T c_{pi}^* dT \quad (31.13)$$

$$s_i^0 = s_{0i}^0 + \int_{T_0}^T \frac{c_{pi}^*}{T} dT \quad (31.14)$$

(32) **General Equations for the Thermodynamic Properties of Gas Mixtures in Terms of  $V$  and  $T$ :** The relations derived in Section 30 follow:

$$E = \int_V^\infty \left[ p - T \left( \frac{\partial p}{\partial T} \right)_{Vn} \right] dV + (\Sigma_i n_i e_i^0) \quad (32.1)$$

$$H = \int_V^\infty \left[ p - T \left( \frac{\partial p}{\partial T} \right)_{Vn} \right] dV + pV + (\Sigma_i n_i e_i^0) \quad (32.2)$$

$$S = \int_V^\infty \left[ \frac{(\Sigma_i n_i)R}{V} - \left( \frac{\partial p}{\partial T} \right)_{Vn} \right] dV + \left( \Sigma_i n_i R \ln \frac{V}{n_i R T} \right) + (\Sigma_i n_i s_i^0) \quad (32.3)$$

$$A = \int_V^\infty \left[ p - \frac{(\Sigma_i n_i)RT}{V} \right] dV - \left( \Sigma_i n_i R T \ln \frac{V}{n_i R T} \right) + [\Sigma_i n_i (e_i^0 - T s_i^0)] \quad (32.4)$$

$$F = \int_V^\infty \left[ p - \frac{(\Sigma_i n_i)RT}{V} \right] dV - \left( \Sigma_i n_i R T \ln \frac{V}{n_i R T} \right) + pV + [\Sigma_i n_i (e_i^0 - T s_i^0)] \quad (32.5)$$

$$\mu_i = \int_V^\infty \left[ \left( \frac{\partial p}{\partial n_i} \right)_{VTn} - \frac{RT}{V} \right] dV - RT \ln \frac{V}{n_i R T} + RT + e_i^0 - T s_i^0 \quad (32.6)$$

$$RT \ln f_i = \int_V^\infty \left[ \left( \frac{\partial p}{\partial n_i} \right)_{VTn} - \frac{RT}{V} \right] dV - RT \ln \frac{V}{n_i R T} \quad (32.7)$$

$$C_p = (\Sigma_i n_i c_{pi}^*) - (\Sigma_i n_i)R - T \frac{(\partial p / \partial T)_{Vn}^2}{(\partial p / \partial V)_{Tn}} - T \int_V^\infty \left( \frac{\partial^2 p}{\partial T^2} \right)_{Vn} dV \quad (32.8)$$

$$C_V = (\Sigma_i n_i c_{vi}^*) - T \int_V^\infty \left( \frac{\partial^2 p}{\partial T^2} \right)_{Vn} dV \quad (32.9)$$

$$C_p - C_V = -T \frac{(\partial p / \partial T)_{Vn}^2}{(\partial p / \partial V)_{Tn}} \quad (32.10)$$

$$\mu_{J.T.} C_p = - \frac{T(\partial p / \partial T)_{Vn} + V(\partial p / \partial V)_{Tn}}{(\partial p / \partial V)_{Tn}} \quad (32.11)$$

$$\eta C_V = - T \left[ \frac{\partial(p/T)}{\partial T} \right]_{Vn} \quad (32.12)$$

In the foregoing expressions

$$e_i^0 = e_{0i}^0 + \int_{T_0}^T c_{vi}^* dT \quad (32.13)$$

$$s_i^0 = s_{0i}^0 + \int_{T_0}^T \frac{c_{vi}^*}{T} dT + R \ln \frac{T}{T_0} \quad (32.14)$$

**(33) Integrated Equations for the Thermodynamic Properties of Gas Mixtures in Terms of  $p$  and  $T$ :** The relations of Section 31 can be expressed in terms of the virial parameters of the equation of state (9.15) for gas mixtures:

$$V = \frac{(\sum_i n_i)RT}{p} + \frac{(\sum_i n_i)\beta_m}{RT} + \frac{(\sum_i n_i)\gamma_m}{(RT)^2} p + \frac{(\sum_i n_i)\delta_m}{(RT)^3} p^2$$

The derivatives of the virial parameters are given in Section 10.

$$E = \left[ \beta_m - T \left( \frac{\partial \beta_m}{\partial T} \right)_n \right] \frac{(\sum_i n_i)p}{RT} + \left[ \gamma_m - T \left( \frac{\partial \gamma_m}{\partial T} \right)_n \right] \frac{(\sum_i n_i)p^2}{2(RT)^2} + \left[ \delta_m - T \left( \frac{\partial \delta_m}{\partial T} \right)_n \right] \frac{(\sum_i n_i)p^3}{3(RT)^3} - (\sum_i n_i)RT + (\sum_i n_i)h_i^0 \quad (33.1)$$

$$H = \left[ 2\beta_m - T \left( \frac{\partial \beta_m}{\partial T} \right)_n \right] \frac{(\sum_i n_i)p}{RT} + \left[ 3\gamma_m - T \left( \frac{\partial \gamma_m}{\partial T} \right)_n \right] \frac{(\sum_i n_i)p^2}{2(RT)^2} + \left[ 4\delta_m - T \left( \frac{\partial \delta_m}{\partial T} \right)_n \right] \frac{(\sum_i n_i)p^3}{3(RT)^3} + (\sum_i n_i)h_i^0 \quad (33.2)$$

$$S = - (\sum_i n_i R \ln p x_i) + \left[ \frac{\beta_m}{T} - \left( \frac{\partial \beta_m}{\partial T} \right)_n \right] \frac{(\sum_i n_i)p}{RT} + \left[ 2 \frac{\gamma_m}{T} - \left( \frac{\partial \gamma_m}{\partial T} \right)_n \right] \frac{(\sum_i n_i)p^2}{2(RT)^2} + \left[ 3 \frac{\delta_m}{T} - \left( \frac{\partial \delta_m}{\partial T} \right)_n \right] \frac{(\sum_i n_i)p^3}{3(RT)^3} + (\sum_i n_i)s_i^0 \quad (33.3)$$

$$A = (\sum_i n_i RT \ln p x_i) - \gamma_m \frac{(\sum_i n_i)p^2}{2(RT)^2} + 2\delta_m \frac{(\sum_i n_i)p^3}{3(RT)^3} - (\sum_i n_i)RT + (\sum_i n_i)h_i^0 - T(\sum_i n_i)s_i^0 \quad (33.4)$$

$$F = (\Sigma_i n_i RT \ln p x_i) + \beta_m \frac{(\Sigma_i n_i) p}{RT} + \gamma_m \frac{(\Sigma_i n_i) p^2}{2(RT)^2} \\ + \delta_m \frac{(\Sigma_i n_i) p^3}{3(RT)^3} + (\Sigma_i n_i h_i^0) - T(\Sigma_i n_i s_i^0) \quad (33.5)$$

$$\mu_i = RT \ln p x_i + \left[ \beta_m + (\Sigma_i n_i) \left( \frac{\partial \beta_m}{\partial n_i} \right)_{T_n} \right] \frac{p}{RT} \\ + \left[ \gamma_m + (\Sigma_i n_i) \left( \frac{\partial \gamma_m}{\partial n_i} \right)_{T_n} \right] \frac{p^2}{2(RT)^2} \\ + \left[ \delta_m + (\Sigma_i n_i) \left( \frac{\partial \delta_m}{\partial n_i} \right)_{T_n} \right] \frac{p^3}{3(RT)^3} + h_i^0 - T s_i^0 \quad (33.6)$$

$$RT \ln f_i = RT \ln p x_i + \left[ \beta_m + (\Sigma_i n_i) \left( \frac{\partial \beta_m}{\partial n_i} \right)_{T_n} \right] \frac{p}{RT} \\ + \left[ \gamma_m + (\Sigma_i n_i) \left( \frac{\partial \gamma_m}{\partial n_i} \right)_{T_n} \right] \frac{p^2}{2(RT)^2} \\ + \left[ \delta_m + (\Sigma_i n_i) \left( \frac{\partial \delta_m}{\partial n_i} \right)_{T_n} \right] \frac{p^3}{3(RT)^3} \quad (33.7)$$

$$C_p = (\Sigma_i n_i c_{pi}^*) - \left[ 2 \frac{\beta_m}{T} - 2 \left( \frac{\partial \beta_m}{\partial T} \right)_n + T \left( \frac{\partial^2 \beta_m}{\partial T^2} \right)_n \right] \frac{(\Sigma_i n_i) p}{RT} \\ - \left[ 6 \frac{\gamma_m}{T} - 4 \left( \frac{\partial \gamma_m}{\partial T} \right)_n + T \left( \frac{\partial^2 \gamma_m}{\partial T^2} \right)_n \right] \frac{(\Sigma_i n_i) p^2}{2(RT)^2} \\ - \left[ 12 \frac{\delta_m}{T} - 6 \left( \frac{\partial \delta_m}{\partial T} \right)_n + T \left( \frac{\partial^2 \delta_m}{\partial T^2} \right)_n \right] \frac{(\Sigma_i n_i) p^3}{3(RT)^3} \quad (33.8)$$

$$C_v = (\Sigma_i n_i c_{vi}^*) + (\Sigma_i n_i) R \\ (\Sigma_i n_i) T \left\{ R - \left[ \frac{\beta_m}{T} - \left( \frac{\partial \beta_m}{\partial T} \right)_n \right] \frac{p}{RT} \right. \\ \left. - \left[ 2 \frac{\gamma_m}{T} - \left( \frac{\partial \gamma_m}{\partial T} \right)_n \right] \frac{p^2}{(RT)^2} - \left[ 3 \frac{\delta_m}{T} - \left( \frac{\partial \delta_m}{\partial T} \right)_n \right] \frac{p^3}{(RT)^3} \right\} \\ - \left[ 2 \frac{\beta_m}{T} - 2 \left( \frac{\partial \beta_m}{\partial T} \right)_n + T \left( \frac{\partial^2 \beta_m}{\partial T^2} \right)_n \right] \frac{(\Sigma_i n_i) p}{RT} \\ - \left[ 6 \frac{\gamma_m}{T} - 4 \left( \frac{\partial \gamma_m}{\partial T} \right)_n + T \left( \frac{\partial^2 \gamma_m}{\partial T^2} \right)_n \right] \frac{(\Sigma_i n_i) p^2}{2(RT)^2} \\ - \left[ 12 \frac{\delta_m}{T} - 6 \left( \frac{\partial \delta_m}{\partial T} \right)_n + T \left( \frac{\partial^2 \delta_m}{\partial T^2} \right)_n \right] \frac{(\Sigma_i n_i) p^3}{3(RT)^3} \quad (33.9)$$

$$\begin{aligned}
 C_p - C_v &= (\sum_i n_i) T \left\{ R - \left[ \frac{\beta_m}{T} - \left( \frac{\partial \beta_m}{\partial T} \right)_n \right] \frac{p}{RT} \right. \\
 &\quad \left. - \left[ 2\gamma_m - \left( \frac{\partial \gamma_m}{\partial T} \right)_n \right] \frac{p^2}{(RT)^2} - \left[ 3\frac{\delta_m}{T} - \left( \frac{\partial \delta_m}{\partial T} \right)_n \right] \frac{p^3}{(RT)^3} \right\} \\
 &\quad - \frac{RT - \gamma_m}{(RT)^2} - \frac{2\delta_m}{(RT)^3}
 \end{aligned} \quad (33.10)$$

$$\begin{aligned}
 \mu_{J.T.} C_p &= - \left[ 2\beta_m - T \left( \frac{\partial \beta_m}{\partial T} \right)_n \right] \frac{(\sum_i n_i)}{RT} \\
 &\quad - \left[ 3\gamma_m - T \left( \frac{\partial \gamma_m}{\partial T} \right)_n \right] \frac{(\sum_i n_i) p}{(RT)} \\
 &\quad - \left[ 4\delta_m - T \left( \frac{\partial \delta_m}{\partial T} \right)_n \right] \frac{(\sum_i n_i) p^2}{(RT)^2}
 \end{aligned} \quad (33.11)$$

$$\begin{aligned}
 \eta C_v &= - \left[ \beta_m - T \left( \frac{\partial \beta_m}{\partial T} \right)_n \right] \frac{p^2}{RT} - \left[ \gamma_m - T \left( \frac{\partial \gamma_m}{\partial T} \right)_n \right] \frac{p^3}{(RT)^2} \\
 &\quad - \left[ \delta_m - T \left( \frac{\partial \delta_m}{\partial T} \right)_n \right] \frac{p^4}{(RT)^3} \\
 &\quad - \frac{RT - \gamma_m}{(RT)^2} - \frac{2\delta_m}{(RT)^3}
 \end{aligned} \quad (33.12)$$

(34) **Integrated Equations for the Thermodynamic Properties of Gas Mixtures in Terms of  $V$  and  $T$ :** The general relations of Section 32 can be expressed in terms of the virial parameters of Equation (9.12) for gas mixtures:

$$p = \frac{(\sum_i n_i) RT}{V} + \frac{(\sum_i n_i)^2 \beta_m}{V^2} + \frac{(\sum_i n_i)^3 \gamma_m}{V^3} + \frac{(\sum_i n_i)^4 \delta_m}{V^4}$$

The derivatives of the virial parameters are given in Section 10.

$$\begin{aligned}
 E &= \left[ \beta_m - T \left( \frac{\partial \beta_m}{\partial T} \right)_n \right] \frac{(\sum_i n_i)^2}{V} \\
 &\quad + \left[ \gamma_m - T \left( \frac{\partial \gamma_m}{\partial T} \right)_n \right] \frac{(\sum_i n_i)^3}{2V^2} \\
 &\quad + \left[ \delta_m - T \left( \frac{\partial \delta_m}{\partial T} \right)_n \right] \frac{(\sum_i n_i)^4}{3V^3} + (\sum_i n_i e_i^0)
 \end{aligned} \quad (34.1)$$

$$\begin{aligned}
 H &= \left[ 2\beta_m - T \left( \frac{\partial \beta_m}{\partial T} \right)_n \right] \frac{(\sum_i n_i)^2}{V} \\
 &\quad + \left[ 3\gamma_m - T \left( \frac{\partial \gamma_m}{\partial T} \right)_n \right] \frac{(\sum_i n_i)^3}{2V^2} \\
 &\quad + \left[ 4\delta_m - T \left( \frac{\partial \delta_m}{\partial T} \right)_n \right] \frac{(\sum_i n_i)^4}{3V^3} \\
 &\quad + (\sum_i n_i) RT + (\sum_i n_i e_i^0)
 \end{aligned} \quad (34.2)$$

$$S = \left( \sum_i n_i R \ln \frac{V}{n_i R T} \right) - \left( \frac{\partial \beta_m}{\partial T} \right)_n \frac{(\sum_i n_i)^2}{V} \\ - \left( \frac{\partial \gamma_m}{\partial T} \right)_n \frac{(\sum_i n_i)^3}{2V^2} - \left( \frac{\partial \delta_m}{\partial T} \right)_n \frac{(\sum_i n_i)^4}{3V^3} + (\sum_i n_i s_i^0) \quad (34.3)$$

$$A = - \left( \sum_i n_i R T \ln \frac{V}{n_i R T} \right) + \beta_m \frac{(\sum_i n_i)^2}{V} \\ + \gamma_m \frac{(\sum_i n_i)^3}{2V^2} + \delta_m \frac{(\sum_i n_i)^4}{3V^3} + (\sum_i n_i e_i^0) - T(\sum_i n_i s_i^0) \quad (34.4)$$

$$F = - \left( \sum_i n_i R T \ln \frac{V}{n_i R T} \right) + 2\beta_m \frac{(\sum_i n_i)^2}{V} + 3\gamma_m \frac{(\sum_i n_i)^3}{2V^2} \\ + 4\delta_m \frac{(\sum_i n_i)^4}{3V^3} + (\sum_i n_i) R T + (\sum_i n_i e_i^0) - T(\sum_i n_i s_i^0) \quad (34.5)$$

$$\mu_i = - R T \ln \frac{V}{n_i R T} + \left[ 2\beta_m + (\sum_i n_i) \left( \frac{\partial \beta_m}{\partial n_i} \right)_{T,n} \right] \frac{(\sum_i n_i)}{V} \\ + \left[ 3\gamma_m + (\sum_i n_i) \left( \frac{\partial \gamma_m}{\partial n_i} \right)_{T,n} \right] \frac{(\sum_i n_i)^2}{2V^2} \\ + \left[ 4\delta_m + (\sum_i n_i) \left( \frac{\partial \delta_m}{\partial n_i} \right)_{T,n} \right] \frac{(\sum_i n_i)^3}{3V^3} + e_i^0 - T s_i^0 \quad (34.6)$$

$$R T \ln f_i = - R T \ln \frac{V}{n_i R T} + \left[ 2\beta_m + (\sum_i n_i) \left( \frac{\partial \beta_m}{\partial n_i} \right)_{T,n} \right] \frac{(\sum_i n_i)}{V} \\ + \left[ 3\gamma_m + (\sum_i n_i) \left( \frac{\partial \gamma_m}{\partial n_i} \right)_{T,n} \right] \frac{(\sum_i n_i)^2}{2V^2} \\ + \left[ 4\delta_m + (\sum_i n_i) \left( \frac{\partial \delta_m}{\partial n_i} \right)_{T,n} \right] \frac{(\sum_i n_i)^3}{3V^3} \quad (34.7)$$

$$C_p = (\sum_i n_i c_{pi}^*) - (\sum_i n_i) R \\ (\sum_i n_i) T \left\{ R + \left( \frac{\partial \beta_m}{\partial T} \right)_n \frac{(\sum_i n_i)}{V} \right. \\ \left. + \left( \frac{\partial \gamma_m}{\partial T} \right)_n \frac{(\sum_i n_i)^2}{V^2} + \left( \frac{\partial \delta_m}{\partial T} \right)_n \frac{(\sum_i n_i)^3}{V^3} \right\} \\ - T \left( \frac{\partial^2 \beta_m}{\partial T^2} \right)_n \frac{(\sum_i n_i)^2}{V} - T \left( \frac{\partial^2 \gamma_m}{\partial T^2} \right)_n \frac{(\sum_i n_i)^3}{2V^2} \\ - T \left( \frac{\partial^2 \delta_m}{\partial T^2} \right)_n \frac{(\sum_i n_i)^4}{3V^3} \quad (34.8)$$

$$C_V = (\Sigma_i n_i c_{vi}^*) - T \left( \frac{\partial^2 \beta_m}{\partial T^2} \right)_n \frac{(\Sigma_i n_i)^2}{V} \\ - T \left( \frac{\partial^2 \gamma_m}{\partial T^2} \right)_n \frac{(\Sigma_i n_i)^3}{2V^2} - T \left( \frac{\partial^2 \delta_m}{\partial T^2} \right)_n \frac{(\Sigma_i n_i)^4}{3V^3} \quad (34.9)$$

$$(\Sigma_i n_i) T \left\{ R + \left( \frac{\partial \beta_m}{\partial T} \right)_n \frac{(\Sigma_i n_i)}{V} \right. \\ \left. + \left( \frac{\partial \gamma_m}{\partial T} \right)_n \frac{(\Sigma_i n_i)^2}{V^2} + \left( \frac{\partial \delta_m}{\partial T} \right)_n \frac{(\Sigma_i n_i)^3}{V^3} \right\} \\ C_p - C_V \quad RT + 2\beta_m \frac{(\Sigma_i n_i)}{V} + 3\gamma_m \frac{(\Sigma_i n_i)^2}{V^2} + 4\delta_m \frac{(\Sigma_i n_i)^3}{V^3} \quad (34.10)$$

$$\mu_{J.T.} C_p = \frac{- \left[ 2\beta_m - T \left( \frac{\partial \beta_m}{\partial T} \right)_n \right] (\Sigma_i n_i) - \left[ 3\gamma_m - T \left( \frac{\partial \gamma_m}{\partial T} \right)_n \right] \frac{(\Sigma_i n_i)^2}{V} - \left[ 4\delta_m - T \left( \frac{\partial \delta_m}{\partial T} \right)_n \right] \frac{(\Sigma_i n_i)^3}{V^2}}{RT + 2\beta_m \frac{(\Sigma_i n_i)}{V} + 3\gamma_m \frac{(\Sigma_i n_i)^2}{V^2} + 4\delta_m \frac{(\Sigma_i n_i)^3}{V^3}} \quad (34.11)$$

$$\eta C_V = - \left[ \beta_m - T \left( \frac{\partial \beta_m}{\partial T} \right)_n \right] \frac{(\Sigma_i n_i)^2}{V^2} \\ - \left[ \gamma_m - T \left( \frac{\partial \gamma_m}{\partial T} \right)_n \right] \frac{(\Sigma_i n_i)^3}{V^3} \\ - \left[ \delta_m - T \left( \frac{\partial \delta_m}{\partial T} \right)_n \right] \frac{(\Sigma_i n_i)^4}{V^4} \quad (34.12)$$

(35) **Integrated Approximate Equations for the Thermodynamic Properties of Gas Mixtures in Terms of  $p$  and  $T$ :** The following approximate equations for gas mixtures correspond to those given for pure gases in Section 22. The values of the parameters  $A_{0m}$ ,  $B_{0m}$ ,  $c_m$  for the mixture are

$$A_{0m} = (\Sigma_i x_i A_{0i}^{1/2})^2 \\ B_{0m} = \frac{1}{8} \Sigma_i \Sigma_j x_i x_j (B_{0i}^{1/3} + B_{0j}^{1/3})^3 = \frac{1}{4} (\Sigma_i x_i B_{0i}) + \frac{3}{4} (\Sigma_i x_i B_{0i}^{1/3}) (\Sigma_i x_i B_{0i}^{2/3}) \\ c_m = (\Sigma_i x_i c_i^{1/2})^2 \\ E = - \left[ \frac{A_{0m}}{RT} + \frac{3c_m}{T^3} \right] (\Sigma_i n_i) p - (\Sigma_i n_i) RT + (\Sigma_i n_i h_i^0) \quad (35.1)$$

$$H = \left[ B_{0m} - \frac{2A_{0m}}{RT} - \frac{4c_m}{T^3} \right] (\Sigma_i n_i) p + (\Sigma_i n_i h_i^0) \quad (35.2)$$

$$S = - (\Sigma_i n_i R \ln p x_i) - \left[ \frac{A_{0m}}{RT^2} + \frac{3c_m}{T^4} \right] (\Sigma_i n_i) p + (\Sigma_i n_i s_i^0) \quad (35.3)$$



$$A = (\Sigma_i n_i RT \ln p x_i) - (\Sigma_i n_i) RT + (\Sigma_i n_i h_i^0) - T(\Sigma_i n_i s_i^0) \quad (35.4)$$

$$F = (\Sigma_i n_i RT \ln p x_i) + \left[ B_{0m} - \frac{A_{0m}}{RT} - \frac{c_m}{T^3} \right] (\Sigma_i n_i) p \\ + (\Sigma_i n_i h_i^0) - T(\Sigma_i n_i s_i^0) \quad (35.5)$$

$$\mu_i = RT \ln p x_i + \left[ \frac{\beta_i}{RT} + \frac{D_i(\beta)}{RT} \right] p + h_i^0 - T s_i^0 \\ = RT \ln p x_i + \left\{ \left[ B_{0i} - \frac{A_{0i}}{RT} - \frac{c_i}{T^3} \right] \right. \\ \left. - \left[ \frac{3}{4} (B_{0i}^{1/3} - \Sigma_i x_i B_{0i}^{1/3}) (B_{0i}^{2/3} - \Sigma_i x_i B_{0i}^{2/3}) \right. \right. \\ \left. \left. \frac{(A_{0i}^{1/2} - \Sigma_i x_i A_{0i}^{1/2})^2}{RT} \quad \frac{(c_i^{1/2} - \Sigma_i x_i c_i^{1/2})^2}{T^3} \right] \right\} p + h_i^0 - T s_i^0 \quad (35.6)$$

$$RT \ln f_i = RT \ln p x_i + \left[ \frac{\beta_i}{RT} + \frac{D_i(\beta)}{RT} \right] p \quad (35.7)$$

$$C_p = (\Sigma_i n_i c_{pi}^*) + \left[ \frac{2A_{0m}}{RT^2} + \frac{12c_m}{T^4} \right] (\Sigma_i n_i) p \quad (35.8)$$

$$C_V = (\Sigma_i n_i c_{vi}^*) + \frac{6c_m}{T^4} (\Sigma_i n_i) p \quad (35.9)$$

$$C_p - C_V = (\Sigma_i n_i) R + \left[ \frac{2A_{0m}}{RT^2} + \frac{6c_m}{T^4} \right] (\Sigma_i n_i) p \quad (35.10)$$

$$\mu_{J.T.} C_p = - \left[ B_{0m} - \frac{2A_{0m}}{RT} - \frac{4c_m}{T^3} \right] (\Sigma_i n_i) \\ + \left[ \frac{2B_{0m} b_m}{RT} - \frac{3A_{0m} a_m}{(RT)^2} + \frac{5B_{0m} c_m}{RT^4} \right] (\Sigma_i n_i) p \quad (35.11)$$

$$\eta C_V = - \left[ \frac{A_{0m}}{(RT)^2} + \frac{3c_m}{RT^4} \right] p^2 \quad (35.12)$$

(36) **Equilibrium Pressure and Equilibrium Concentration of a Gas in a Mixture:** When a pure gas is in isothermal equilibrium with a gas mixture through a membrane permeable to that gas alone, the chemical potential of the substance is the same in both phases. Let the gas in the mixture be distinguished by the subscript  $i$  and the same gas when pure by  $k$ . The pressure and concentration of the pure gas under these circumstances are actually properties of the gas in the mixture and may be called the equilibrium pressure  $p_{ek}$  and equilibrium concentration  $C_{ek}$  of the gas  $i$  in the mixture.

Equations (18.6) and (31.6) express the chemical potential of a pure gas and of a gas in a mixture in terms of pressure as one of the independent vari-

ables, whereas (19.6) and (32.6) are the corresponding equations with volume as one of the independent variables. Equating the two expressions for the chemical potentials in terms of the same set of independent variables, we find the expression (36.1) given below for the ratio of the equilibrium pressure  $p_{ek}$  of a gas in a mixture to its partial pressure  $px_i$ , and (36.5) for the ratio of the equilibrium concentration  $C_{ek}$  of a gas in a mixture to its concentrations  $C_i (= Cx_i)$  in the mixture. In each expression the first integral on the right-hand side is to be evaluated for the gas mixture at the temperature  $T$  of the calculation; and the second for the pure gas.

In Equations (36.2) and (36.6) the integrals have been expressed in terms of the virial parameters of the equation of state (6.1) or (6.3) for the pure gas and (9.12) or (9.15) for the gas mixture. Equations (36.3) and (36.7) express the derivatives in terms of the quantities defined in Section 10. In general the equilibrium pressure or concentration is not computed for its own sake but as an intermediate step in the calculation of the mass-action function of a chemical reaction or of the equilibrium conditions among two or more phases. In these cases we obtain very accurate results if we drop all terms on the right-hand sides of Equations (36.3) and (36.7), except those enclosed in the first pairs of brackets, which give expressions exact to terms of the order of  $p$  or  $C$ . Then the equation of state constants listed in Table II may be used in either relation, and the calculation may be systematized in the manner indicated in Table III. Equations (36.4) and (36.8) give these approximate expressions for  $p_{ek}/px_i$  and  $C_{ek}/C_i$  in terms of the equation of state constants.

$$RT \ln \frac{p_{ek}}{px_i} = \int_0^p \left[ \left( \frac{\partial V}{\partial n_i} \right)_{pTn} - \frac{RT}{p} \right] dp - \int_0^{p_{ek}} \left[ \frac{V_k}{n_k} - \frac{RT}{p_k} \right] dp_k$$

$$(i \equiv k = 1, 2, \dots) \quad (36.1)$$

$$\ln \frac{p_{ek}}{px_i} = \left\{ \left[ \frac{\beta_m}{RT} + \frac{(\Sigma_i n_i)}{RT} \left( \frac{\partial \beta_m}{\partial n_i} \right)_{Tn} \right] \frac{p}{RT} - \frac{\beta_k}{RT} \frac{p_{ek}}{RT} \right\}$$

$$+ \left\{ \left[ \frac{\gamma_m}{RT} + \frac{(\Sigma_i n_i)}{RT} \left( \frac{\partial \gamma_m}{\partial n_i} \right)_{Tn} \right] \frac{p^2}{2(RT)^2} - \frac{\gamma_k}{RT} \frac{p_{ek}^2}{2(RT)^2} \right.$$

$$\left. \left[ \left[ \frac{\delta_m}{RT} + \frac{(\Sigma_i n_i)}{RT} \left( \frac{\partial \delta_m}{\partial n_i} \right)_{Tn} \right] \frac{\delta_k}{RT} \frac{p_{ek}^3}{3(RT)^3} \right] \right\} \quad (36.2)$$

$$\ln \frac{p_{ek}}{px_i} = \left\{ \frac{\beta_k}{RT} \left( \frac{p}{RT} - \frac{p_{ek}}{RT} \right) + \frac{D_i(\beta)}{RT} \frac{p}{RT} \right.$$

$$+ \left\{ \frac{\gamma_k}{RT} \left( \frac{p^2}{2(RT)^2} - \frac{p_{ek}^2}{2(RT)^2} \right) + \frac{[D_i(\gamma) - \gamma_m]}{RT} \frac{p^2}{2(RT)^2} \right\}$$

$$+ \left\{ \frac{\delta_k}{RT} \left( \frac{p^3}{3(RT)^3} - \frac{p_{ek}^3}{3(RT)^3} \right) + \frac{[D_i(\delta) - 2\delta_m]}{RT} \frac{p^3}{3(RT)^3} \right\} \quad (36.3)$$

$$\ln \frac{p_{ek}}{px_i} = \left[ B_{0k} - \frac{A_{0k}}{RT} - \frac{c_k}{T^3} \right] \left( \frac{p - p_{ek}}{RT} \right) - \left[ \frac{3}{4} (B_{0k}^{1/3} - \Sigma_i x_i B_{0i}^{1/3}) (B_{0k}^{2/3} - \Sigma_i x_i B_{0i}^{2/3}) - \frac{(A_{0k}^{1/2} - \Sigma_i x_i A_{0i}^{1/2})^2}{RT} - \frac{(c_k^{1/2} - \Sigma_i x_i c_i^{1/2})^2}{T^3} \right] \frac{p}{RT} \quad (36.4)$$

$$RT \ln \frac{C_{ek}}{C_i} = \int_V^\infty \left[ \left( \frac{\partial p}{\partial n_i} \right)_{V, T, n} - \frac{RT}{V} \right] dV - \int_V^\infty \left[ \left( \frac{\partial p_k}{\partial n_k} \right)_{V, k, T} - \frac{RT}{V_k} \right] dV_k \quad (i \equiv k = 1, 2, \dots) \quad (36.5)$$

$$\ln \frac{C_{ek}}{C_i} = \left\{ \left[ \frac{2\beta_m}{RT} + \frac{(\Sigma_i n_i)}{RT} \left( \frac{\partial \beta_m}{\partial n_i} \right)_{T, n} \right] C - \frac{2\beta_k}{RT} C_{ek} \right\} + \left\{ \left[ \frac{3\gamma_m}{RT} + \frac{(\Sigma_i n_i)}{RT} \left( \frac{\partial \gamma_m}{\partial n_i} \right)_{T, n} \right] \frac{C^2}{2} - \frac{3\gamma_k}{RT} \frac{C_{ek}^2}{2} \right\} + \left\{ \left[ \frac{4\delta_m}{RT} + \frac{(\Sigma_i n_i)}{RT} \left( \frac{\partial \delta_m}{\partial n_i} \right)_{T, n} \right] \frac{C^3}{3} - \frac{4\delta_k}{RT} \frac{C_{ek}^3}{3} \right\} \quad (36.6)$$

$$\ln \frac{C_{ek}}{C_i} = \left\{ \frac{\beta_k}{RT} (C - 2C_{ek}) + \frac{[D_i(\beta) + \beta_m]}{RT} C \right\} + \left\{ \frac{\gamma_k}{RT} \left( \frac{C^2 - 3C_{ek}^2}{2} \right) + \frac{[D_i(\gamma) + \gamma_m]}{RT} \frac{C^2}{2} \right\} + \left\{ \frac{\delta_k}{RT} \left( \frac{C^3 - 4C_{ek}^3}{3} \right) + \frac{[D_i(\delta) + \delta_m]}{RT} \frac{C^3}{3} \right\} \quad (36.7)$$

$$\ln \frac{C_{ek}}{C_i} = \left[ B_{0k} - \frac{A_{0k}}{RT} - \frac{c_k}{T^3} \right] (C - 2C_{ek}) - \left[ \frac{1}{4} (B_{0k} - \Sigma_i x_i B_{0i}) + \frac{1}{4} B_{0k}^{2/3} (B_{0k}^{1/3} - 3\Sigma_i x_i B_{0i}^{1/3}) + \frac{1}{4} B_{0k}^{1/3} (B_{0k}^{2/3} - 3\Sigma_i x_i B_{0i}^{2/3}) - \frac{A_{0k}^{1/2} (A_{0k}^{1/2} - 2\Sigma_i x_i A_{0i}^{1/2})}{RT} - \frac{c_k^{1/2} (c_k^{1/2} - \Sigma_i x_i c_i^{1/2})}{T^3} \right] C \quad (36.8)$$

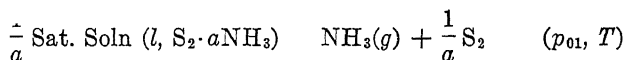
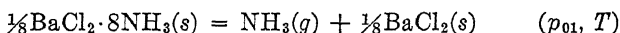
To compute the equilibrium pressure  $p_{ek}$  of a gas in a mixture given the total pressure  $p$  and the composition  $x_1, x_2, \dots$  of the mixture, place  $p_{ek}$  on the right-hand side of any one of the Equations (36.2) to (36.4) equal to its ideal gas value,  $px_i$ , for the first approximation. Then repeat the calculation with the provisional value of  $p_{ek}$  resulting from the first approximation. Usually a third approximation is unnecessary. The equilibrium concentration  $C_{ek}$  can now be calculated from the equation of state (6.3) of the pure gas.

To compute the composition of a mixture of  $m$  gases given the total pressure and  $(m - 1)$  equilibrium pressures, use the ideal gas values  $x_i = p_{ek}/p$  for the mole fractions occurring on the right-hand side of Equations (36.2) to (36.4). Then repeat with the resulting provisional values.

Similarly, given the concentration  $C$  and composition of the mixture, we can evaluate the equilibrium concentration  $C_{ek}$  from any one of the Equations (36.6) to (36.8). If desired, the complete equation can be used with the equation of state constants given in Table III. For the first approximation, place  $C_{ek}$  equal to  $Cx_i$ . The equilibrium pressure can then be found from the equation of state (6.1) of the pure gas.

Also, given the concentration  $C$  of the mixture and  $(m - 1)$  equilibrium concentrations, we can place  $x_i$  on the right-hand side of the equation equal to  $C_{ek}/C$  for the first approximation.

**(37) Effect of Hydrostatic Pressure and of an Inert Gas on a Univariant Equilibrium Involving a Pure Gaseous Phase:** In a univariant equilibrium between a pure gaseous substance  $S_1$  and one or more condensed phases, as



the pressure  $p_{01}$  is a function of temperature alone. We can define<sup>1</sup> the chemical potential  $\mu_{s1}$  and the partial molar volume  $v_{s1}$  of  $S_1$  in the condensed complex by the relations

$$\mu_{s1} = \Delta F_j; \quad v_{s1} = \Delta V_j \quad (37.1)$$

where  $\Delta F_j$  is the increase in free energy, and  $\Delta V_j$  the increase in volume of the condensed complex when one mole of  $S_1$  is absorbed from the gas phase. When only one condensed phase is present  $\mu_{s1}$  is its molar free energy and  $v_{s1}$  is its molar volume.

Now let the condensed phases be subjected to the hydrostatic pressure  $p$ , say by a piston permeable to the gas alone, whereby the equilibrium pressure  $p_{01}$  is increased to  $p_{e1}$ . For the chemical potential of  $S_1$  in the condensed complex we find

$$\mu_{s1}(p, T) = \mu_{s1}(p_{01}, T) + \int_{p_{01}}^p v_{s1} dp \quad (37.2)$$

where  $\mu_{s1}(p_{01}, T)$  is equal to the chemical potential of the vapor of  $S_1$  at the vapor pressure  $p_{01}$  and is given by Equation (18.6) with  $p$  replaced by  $p_{01}$ . The chemical potential of  $S_1$  in the gas phase when the condensed complex is under the pressure  $p$  is the equilibrium pressure  $p_{e1}$  given by (18.6) with  $p$  replaced by  $p_{e1}$ . Equating the two values of the chemical potential of  $S_1$  gives Equation (37.4) written below.

<sup>1</sup> L. J. Gillespie, *Proc. Amer. Acad. Arts Sci.*, **66**, 153 (1930).

Let

$$v_{s1}(p, T) = v_{s1}^*(0, T)(1 - \kappa_{1p}) \quad (37.3)$$

where  $v_{s1}^*$  is the (extrapolated) value of  $v_{s1}$  at zero pressure and  $\kappa_1$  is the isothermal compressibility of this quantity.

Introduction of the equation of state (6.3) and the relation (37.3) into Equation (37.4) gives (37.5). In general, terms of higher order than the first in pressure may be dropped, and the equation of state constants of Table II or those derived from critical data used. Equation (37.6) expresses  $p_{e1}/p_{01}$  in terms of the equation of state constants: here  $v_{s1}$  may as well be taken for a pressure of one atmosphere or for  $p_{01}$ .

$$RT \ln \frac{p_{e1}}{p_{01}} = - \int_{p_{01}}^{p_{e1}} \left[ \frac{V_1}{n_1} - \frac{RT}{p_1} \right] dp_1 + \int_{p_{01}}^p v_{s1} dp \quad (37.4)$$

$$\begin{aligned} \ln \frac{p_{e1}}{p_{01}} = & - \frac{\beta_1}{RT} \left( \frac{p_{e1} - p_{01}}{RT} \right) - \frac{\gamma_1}{RT} \left( \frac{p_{e1}^2 - p_{01}^2}{2(RT)^2} \right) \\ & - \frac{\delta_1}{RT} \left( \frac{p_{e1}^3 - p_{01}^3}{3(RT)^3} \right) + \frac{v_{s1}^*}{RT} (p - p_{01}) - \frac{\kappa_1}{2RT} (p^2 - p_{01}^2) \end{aligned} \quad (37.5)$$

$$\ln \frac{p_{e1}}{p_{01}} = - \left[ B_{01} - \frac{A_{01}}{RT} - \frac{c_1}{T^3} \right] \left( \frac{p_{e1} - p_{01}}{RT} \right) + \frac{v_{s1}}{RT} (p - p_{01}) \quad (37.6)$$

In using these equations, we can place  $p_{e1}$  equal to  $p_{01}$  on the right-hand side for the first approximation which yields the usual ideal gas integration of the Poynting relation.

Now let a univariant system be in equilibrium under its vapor pressure  $p_{01}$ , and let an inert gas that does not react chemically with the vapor  $S_1$  and is insoluble in the condensed complex be introduced into the system until the total pressure becomes  $p$ , the mole fraction of  $S_1$  in the gas phase being  $x_1$ . The chemical potential of  $S_1$  in the condensed complex is given by Equation (37.2) and in the gas phase by (31.6). The resulting relation for the ratio of the partial pressure  $px_1$  of  $S_1$  in the gas mixture to the vapor pressure  $p_{01}$  before the introduction of the inert gas is (37.7). The first integral of this expression refers to the gas mixture, the second to pure gaseous  $S_1$ , and the third to the condensed complex. The two following equations correspond to (37.5) and (37.6). Equation (37.8) was derived by Gerry and Gillespie<sup>2</sup> and applied to the calculation of the normal vapor pressure of iodine from measurements made by the gas current method.

$$\begin{aligned} RT \ln \frac{px_1}{p_{01}} = & - \int_0^p \left[ \left( \frac{\partial V}{\partial n_1} \right)_{pTn} - \frac{RT}{p} \right] dp \\ & + \int_0^{p_{01}} \left[ \frac{V_1}{n_1} - \frac{RT}{p_1} \right] dp_1 + \int_{p_{01}}^p v_{s1} dp \end{aligned} \quad (37.7)$$

<sup>2</sup> H. T. Gerry and L. J. Gillespie, *Phys. Rev.*, **40**, 269 (1932).

$$\ln \frac{p_{x_1}}{p_{01}} = \left\{ \left( v_{s1}^* - \frac{\beta_1}{RT} \right) \left( \frac{p - p_{01}}{RT} \right) - \frac{D_1(\beta)}{RT} \frac{p}{R'} \right. \\ \left. - \left\{ \left( RT\kappa_1 + \frac{\gamma_1}{RT} \right) \left( \frac{p^2 - p_{01}^2}{2(RT)^2} \right) + \frac{[D_1(\gamma) - \gamma_m]}{RT} \frac{p^2}{2(RT)^2} \right. \right. \\ \left. \left. - \left\{ \frac{\delta_1}{RT} \left( \frac{p^3 - p_{01}^3}{3(RT)^3} \right) + \frac{[D_1(\delta) - 2\delta_m]}{RT} \frac{p^3}{3(RT)^3} \right\} \right\} \right. \quad (37.8)$$

$$\left[ v_{s1} - \left( B_{01} - \frac{A_{01}}{RT} - \frac{c_1}{T^3} \right) \right] \left( \frac{p - p_{01}}{RT} \right) \\ + \left[ \frac{3}{4} (B_{01}^{1/3} - \sum_i x_i B_{0i}^{1/3}) (B_{01}^{2/3} - \sum_i x_i B_{0i}^{2/3}) \right. \\ \left. \frac{(A_{01}^{1/2} - \sum_i x_i A_{0i}^{1/2})^2}{RT} \frac{(c_1^{1/2} - \sum_i x_i c_i^{1/2})^2}{T^3} \right] \frac{p}{RT} \quad (37.9)$$

(38) **Chemical Potential of a Volatile Constituent of a Condensed Phase:**

For the discussion of the equilibrium between condensed and gaseous phases we need a relation for the chemical potential of a constituent of a condensed phase. The activity coefficient  $\alpha_i$  of the constituent  $i$  at a mole fraction  $y_i$  in a solution (liquid or solid) at the pressure  $p$  and temperature  $T$  is defined by the relation

$$\mu_{si}(p, T, y_i) = RT \ln y_i + RT \ln \alpha_i(p, T, y_i) + \mu_{si}^0(p, T) \quad (38.1)$$

where  $\mu_{si}(p, T, y_i)$  is the chemical potential of  $i$  in the state  $p, T, y_i$ , and  $\mu_{si}^0(p, T)$  is an integration constant determined by the statement that  $\alpha_i = 1$  in the arbitrarily selected reference state. In the following treatment  $p$  is always the vapor pressure of the solution.

The most convenient choice of reference state for the present problem is the following. Irrespective of the designation of the substance  $S_i$  as solvent or solute, we may select the pure condensed substance ( $y_i = 1$ ) under the vapor pressure  $p$  of the solution at each temperature  $T$  as the reference state of unit activity coefficient ( $\alpha_i = 1$ ). In this state its chemical potential by Equation (38.1) is  $\mu_{si}^0(p, T)$ , and this is given for any pressure  $p$  by the expression

$$\mu_{si}^0(p, T) = \mu_{si}^0(p_{0i}, T) + \int_{p_{0i}}^p v_{si} dp \quad (38.2)$$

where  $\mu_{si}^0(p_{0i}, T)$  is the chemical potential of the pure substance under its vapor pressure  $p_{0i}$  at  $T$  and  $v_{si}$  is its molar volume. But  $\mu_{si}^0(p_{0i}, T)$  is equal to the chemical potential of the vapor at  $p_{0i}$  and  $T$ ; and this is given by Equation (18.6) with  $p$  replaced by  $p_{0i}$ . Making this substitution in Equation (38.2)

and inserting the resulting relation for  $\mu_{si}^0(p, T)$  into (38.1), we find

$$\mu_{si}(p, T, y_i) = RT \ln p_{0i} y_i + RT \ln \alpha_i + \int_{p_{0i}}^p v_{si} dp + \int_0^{p_{0i}} \left[ \frac{V}{n} - \frac{RT}{p} \right] dp + h_i^0 - Ts_i^0 \quad (38.3)$$

where  $h_i^0$  and  $s_i^0$  are temperature functions for the gas given in Section 18. The first integral refers to the pure condensed substance  $i$ , and the second to the pure gaseous substance  $i$ .

In view of Equation (18.7) we can write (38.3) in the form

$$\mu_{si}(p, T, y_i) = RT \ln f_{0i} y_i + RT \ln \alpha_i + \int_{p_{0i}}^p v_{si} dp + h_i^0 - Ts_i^0 \quad (38.4)$$

where  $f_{0i}$  is the fugacity of the constituent  $i$  of  $p_{0i}$  and  $T$ .

We can express  $v_{si}$  by Equation (37.3) for evaluation of the integral of (38.3) and (38.4).

**(39) Chemical Potentials of Pure Condensed Phases:** If the condensed phase is a pure substance  $S_j$  we can select as the standard state the same pressure  $p_0$  and temperature  $T_0$  as for a gas. At any other pressure  $p$  and temperature  $T$  we find for the chemical potential  $\mu_j$

$$\mu_j(p, T) = \int_{T_0}^T v_{sj} dp + h_j^0 - Ts_j^0 \quad (39.1)$$

$$\left. \begin{aligned} h_j^0 &= h_{0j}^0 + \int_{T_0}^T c_{pj} dT \\ s_j^0 &= s_{0j}^0 + \int_{T_0}^T \frac{c_{pj}}{T} dT \end{aligned} \right\} \quad (39.2)$$

where  $v_{sj}$  is the molar volume of  $S_j$  at  $T$ ,  $c_{pj}$  its heat capacity at constant pressure  $p_0$ , and  $h_{0j}^0$  and  $s_{0j}^0$  its heat content and entropy at  $p_0$  and  $T_0$ .

**(40) Equilibrium between Condensed and Gaseous Solutions:** When equilibrium subsists with respect to the passage of a component  $i$  from a condensed to a gaseous phase the chemical potential  $\mu_{si}(p, T, y_i)$  of  $i$  in the condensed phase equals the potential  $\mu_i(p, T, x_i)$  in the gaseous phase. A relation for the former is given in Equation (38.3), and for the latter in (31.6). Equating the two values of the potential and solving for the ratio of the partial pressure  $px_i$  in the gas phase ( $p$ , total pressure;  $x_i$ , mole fraction in gas phase) to the Raoult's law pressure  $p_{0i}y_i$  computed for the condensed phase ( $p_{0i}$ , vapor pressure of pure  $i$ ;  $y_i$  mole fraction in the condensed phase), we obtain Equation (40.1) given below. The first integral of the expression is to be evaluated at  $T$  for the gas mixture, the second for pure gaseous  $i$ , and the third for pure condensed  $i$ .

In Equation (40.2) the integrals of (40.1) are expressed in terms of the virial parameters of (9.15) for the gas mixture and (6.3) for the pure gas, see Section 10, and of the compressibility as defined in (37.3). In Equation (40.3) terms

of higher order than the pressure are dropped, and the parameters  $\beta_{0m}$  and  $\beta_k$  are expressed in terms of the equation of state constants.

Equation (40.2) has been applied to many systems by Scatchard<sup>1</sup> and his collaborators.

$$RT \ln \frac{px_i}{p_{0i}y_i} = - \int_0^p \left[ \left( \frac{\partial V}{\partial n_i} \right)_{pTn} - \frac{RT}{p} \right] dp + \int_0^{p_{0i}} \left[ \frac{V_k}{n_k} - \frac{RT}{p_k} \right] dp_k \\ + \int_{n_{0i}}^p v_{si} dp + RT \ln \alpha_i \quad (i \equiv k = 1, 2, \dots) \quad (40.1)$$

$$\ln \frac{px_i}{p_{0i}y_i} = \left\{ \left( v_{si}^* - \frac{\beta_i}{RT} \right) \left( \frac{p - p_{0i}}{RT} \right) - \frac{D_i(\beta)}{RT} \frac{p}{RT} \right. \\ \left. - \left\{ \left( RT\kappa_1 + \frac{\gamma_i}{RT} \right) \left( \frac{p^2 - p_{0i}^2}{2(RT)^2} \right) + \frac{[D_i(\gamma) - \gamma_m]}{RT} \frac{p^2}{2(RT)^2} \right\} \right. \\ \left. \frac{\delta_i}{RT} \left( \frac{p^3 - p_{0i}^3}{3(RT)^3} \right) + \frac{[D_i(\delta) - 2\delta_m]}{RT} \frac{p^3}{3(RT)^3} + \ln \alpha_i \right\} \quad (40.2)$$

$$\ln \frac{px_i}{p_{0i}y_i} = \left[ v_{si} - \left( B_{0i} - \frac{A_{0i}}{RT} - \frac{c_i}{T^3} \right) \right] \left( \frac{p - p_{0i}}{RT} \right) \\ + \left[ \frac{3}{4} (B_{0i}^{1/3} - \Sigma_i x_i B_{0i}^{1/3}) (B_{0i}^{2/3} - \Sigma_i x_i B_{0i}^{2/3}) \right. \\ \left. \frac{(A_{0i}^{1/2} - \Sigma_i x_i A_{0i}^{1/2})^2}{RT} \quad \frac{(c_i^{1/2} - \Sigma_i x_i c_i^{1/2})^2}{T^3} \right] \frac{p}{RT} + \ln \alpha_i \quad (40.3)$$

(41) **Mass Action Function for a Homogeneous Gaseous Reaction:** Equation (31.6) expresses the chemical potential of a gas in a mixture in terms of  $p$ ,  $T$ ,  $x_1$ ,  $x_2$ ,  $\dots$ . Application of the general equilibrium condition (25.1) gives a relation containing the logarithm of the mass action function  $K_p$  as defined in (25.2). In a similar manner from (32.6), which expresses the chemical potential in terms of  $C$ ,  $T$ ,  $x_1$ ,  $x_2$ ,  $\dots$ , we find a relation for the logarithm of  $K_C$  as defined in (25.3). These expressions are given below:  $K_p$  being given in terms of  $p$ ,  $T$ ,  $x_1$ ,  $x_2$ ,  $\dots$  and  $K_C$  in terms of  $C$ ,  $T$ ,  $x_1$ ,  $x_2$ ,  $\dots$ . Either equilibrium function may be expressed in terms of the other set of independent variables. Thus, to find  $K_p$  as a function of  $C$ ,  $T$ ,  $x_1$ ,  $x_2$ , we add and subtract the term  $RT \ln px_i$  to the right-hand side of (32.6) before applying the general equilibrium condition; and to find  $K_C$  as a function of  $p$ ,  $T$ ,  $x_1$ ,  $x_2$ ,  $\dots$  we add and subtract the term  $RT \ln (RTn_i/V)$  to the right-hand side of (31.6) before applying the general equilibrium condition.

The quantities  $K_p^*$  and  $K_C^*$  are the values of  $K_p$  and  $K_C$ , respectively, at a very low pressure and are functions of temperature alone and contain the heat content (or energy) and entropy constants of the gases at  $T_0$ .

<sup>1</sup> See, for instance, G. Scatchard, *Chem. Rev.*, **8**, 321 (1931); G. Scatchard and C. L. Raymond, *J. Am. Chem. Soc.*, **60**, 1278 (1938); G. Scatchard, S. E. Wood, and J. M. Mochel, *J. Am. Chem. Soc.*, **62**, 712 (1940).



The integrals of Equation (41.1) are evaluated in (41.7) in terms of the virial parameters and their derivatives given in Section 10. In Equation (41.8) terms of higher order than the first in pressure are dropped, and the equation of state constants are used.

$$\ln \frac{K_p}{K_p^*} = -\frac{1}{RT} \left\{ \sum_i \nu_i \left[ \int_0^p \left[ \left( \frac{\partial V}{\partial n_i} \right)_{pTn} - \frac{RT}{p} \right] dp \right] \right\} \quad (41.1)$$

$$= -\frac{1}{RT} \left\{ \sum_i \nu_i \left[ \int_V^\infty \left[ \left( \frac{\partial p}{\partial n_i} \right)_{VTn} - \frac{RT}{V} \right] dV \right] \right\} + (\sum_i \nu_i) \ln \frac{pV}{(\sum_i n_i)RT} \quad (41.2)$$

$$\ln K_p^* = -\frac{1}{RT} [\sum_i \nu_i (h_i^0 - Ts_i^0)] \quad (41.3)$$

$$\ln \frac{K_c}{K_c^*} = -\frac{1}{RT} \left\{ \sum_i \nu_i \left[ \int_V^\infty \left[ \left( \frac{\partial p}{\partial n_i} \right)_{VTn} - \frac{RT}{p} \right] dV \right] \right\} \quad (41.4)$$

$$= -\frac{1}{RT} \left\{ \sum_i \nu_i \left[ \int_0^p \left[ \left( \frac{\partial V}{\partial n_i} \right)_{pTn} - \frac{RT}{p} \right] dp \right] \right\} - (\sum_i \nu_i) \ln \frac{pV}{(\sum_i n_i)RT} \quad (41.5)$$

$$\ln K_c^* = -\frac{1}{RT} [\sum_i \nu_i (e_i^0 + RT - Ts_i^0 + RT \ln RT)] \quad (41.6)$$

$$\ln \frac{K_p}{K_p^*} = -\frac{\{\sum_i \nu_i [\beta_i + D_i(\beta)]\}}{RT} \frac{p}{RT} - \frac{\{\sum_i \nu_i [\gamma_i + D_i(\gamma) - \gamma_m]\}}{RT} \frac{p^2}{2(RT)^2} - \frac{\{\sum_i \nu_i [\delta_i + D_i(\delta) - 2\delta_m]\}}{RT} \frac{p^3}{3(RT)^3} \quad (41.7)$$

$$\left\{ \frac{(\sum_i \nu_i B_{0i})}{RT} - \frac{(\sum_i \nu_i A_{0i})}{RT} - \frac{(\sum_i \nu_i C_i)}{T^3} \right\} \frac{p}{RT} + \left\{ \frac{3}{4} [\sum_i \nu_i (B_{0i}^{1/3} - \sum_i x_i B_{0i}^{1/3}) (B_{0i}^{2/3} - \sum_i x_i B_{0i}^{2/3})] - \frac{[\sum_i \nu_i (A_{0i}^{1/2} - \sum_i x_i A_{0i}^{1/2})^2]}{RT} - \frac{[\sum_i \nu_i (C_i^{1/2} - \sum_i x_i C_i^{1/2})^2]}{T^3} \right\} \frac{p}{RT} \quad (41.8)$$

$$\ln K_p^* = \frac{1}{R} \left[ \int_{T_0}^T \frac{(\sum_i \nu_i c_{pi}^*)}{T} dT \right] - \frac{1}{RT} \left[ \int_{T_0}^T (\sum_i \nu_i c_{pi}^*) dT \right] - \frac{1}{RT} (\sum_i \nu_i h_{0i}^0) + \frac{1}{R} (\sum_i \nu_i s_{0i}^0) \quad (41.9)$$

$$= \frac{1}{R} \int_{T_0}^T \left[ \int_{T_0}^T (\sum_i \nu_i c_{pi}^*) dT \right] \frac{dT}{T^2} - \frac{1}{RT} (\sum_i \nu_i h_{0i}^0) + \frac{1}{R} (\sum_i \nu_i s_{0i}^0) \quad (41.10)$$

In the foregoing equations all summations extend over all species in the gas mixture, the stoichiometric coefficient  $\nu_i$  being zero for a gas  $i$  that does not enter into the chemical reaction, but  $x_i$  is not zero.

Equations (41.8) and (41.10) express the mass action function  $K_p$  in terms of the pressure, temperature, composition of the equilibrium mixture, the equation of state constants of all gases present, the heat capacities of the gases entering into the reaction, and the heat content and entropy constants at the standard temperature of the gases entering into the reaction. The ideal gas law gives  $K_p$  equal to  $K_p^*$ , a function of temperature only. The Lewis and Randall rule gives the first term enclosed in brackets on the right-hand side of Equation (41.8) and thus predicts that  $K_p$  is a function of pressure and temperature but not of the composition of the equilibrium mixture.

The last two sums of Equation (41.10) may be considered adjustable in the absence of heat content and entropy data on the gases entering into the chemical reaction, but these are the only adjustable constants in the complete expression for  $K_p$ .

All of the measurements of the ammonia synthesis equilibrium to 1,000 atm, including equilibrium mixtures containing argon and those containing no argon, have been correlated<sup>1</sup> by the approximate Equation (41.8), with  $K_p^*$  given by (41.10). In this calculation the less exact linear combination for  $B_{0m}$  and  $c_m$  were used. The  $\Delta H$  for the reaction computed for 0°C from the sum ( $\sum_i \nu_i h_{0i}^0$ ) was in good agreement with that derived by other methods, and the predicted compositions of the equilibrium mixtures agreed within experimental accuracy with the measured values.

Equation (41.8) indicates that the optimum mixture<sup>2</sup> of gases to use in order to produce the largest mole fraction of some product in the equilibrium mixture is not necessarily the stoichiometric proportions, and the optimum composition of the initial mixture will vary with the amounts and kinds of inert gases present.

To compute the composition of an equilibrium mixture from Equation (41.8) given the initial composition, pressure, temperature, and the necessary constants of the pure gases, we first compute  $K_p^*$  (the ideal gas value of  $K_p$ ). From this we compute provisional values of the composition of the equilibrium mixture which, inserted into the right-hand side of Equation (41.8), give a provisional value of  $K_p$  from which a second approximation to the equilibrium composition can be found. In general two approximations are sufficient even at high pressures. Faster convergence is obtained if we use the first term in brackets on the right-hand side of Equation (41.8), which does not contain any composition terms, to find  $K_p$  for the first approximation.

**(42) Mass Action Function for a Gaseous Reaction in a System Containing Pure Condensed Phases:** Equations (39.1) and (39.2) give the chemical potential of a pure condensed substance as a function of pressure and temperature.

<sup>1</sup> L. J. Gillespie and J. A. Beattie, *Phys. Rev.*, **36**, 743, 1008 (1930); *ibid.*, **37**, 655 (1931); *J. Am. Chem. Soc.*, **52**, 4239 (1930).

<sup>2</sup> *Ibid.*

When such substances enter into a reaction, the relations of Section 41 must be modified by the addition to the right-hand side of the equations for  $\ln K_p/K_p^*$  and  $\ln K_C/K_C^*$  of the sum:

$$- \frac{1}{RT} \left\{ \sum_i \nu_i \left[ \int_{p_0}^p v_{s_i} dp \right] \right\} \quad (42.1)$$

and to the right-hand side of the equations for  $K_p^*$  and  $K_C^*$ , the sum

$$- \frac{1}{RT} [\sum_i \nu_i (h_i^0 - Ts_i^0)] \quad (42.2)$$

where  $h_i^0$  and  $s_i^0$  are given by Equations (39.2) and the sums extend over all pure condensed phases entering into the chemical reaction.

(43) **Determination of the Energy, Heat Content, and Entropy Constants:** The interpretation of the heat content and entropy constants  $h_0^0$  and  $s_0^0$  of a gas are given in Section 16, and the energy constant  $e_0^0$  is discussed in Section 17. The evaluation of these constants depends on what changes in state are to be studied and may be made on the basis of the following considerations.

1. When no chemical reaction may occur, we can assign arbitrary values to the molar heat content and energy of each individual substance or indeed to a gas mixture of constant composition. If the temperature is to be considered variable, arbitrary values are assigned only at  $(p_0, T_0)$ , but if the temperature is to be constant in all variations, we can assign an arbitrary value at  $p_0$  and the temperature in question.

The usual practice is to take the pressure of the standard state as one atmosphere. Equations (22.2) and (22.3) are sufficiently accurate at this pressure to permit computation of  $h^0$  and  $s^0$  from the assigned values of  $H$  and  $S$  at one atmosphere pressure and a temperature  $T$ .

2. When chemical reactions may occur among the constituent gases of a system, arbitrary values, say zero, may be assigned to the molar heat content and entropy of all elementary substances in the standard state  $(p_0, T_0)$ . The constants  $h_0^0$  and  $s_0^0$  of such elements as are gases under these conditions may be computed from Equations (22.2) and (22.3); and those of elements that are not gases and of compounds can be calculated from these equations and other thermodynamic data. Thus to determine the heat content and entropy constants of a volatile element that is, however, condensed at one atmosphere and  $T_0$ , we can add to the value zero the small change in these properties for the change in state from one atmosphere to the vapor pressure, then add  $\Delta H$  and  $\Delta S$  of vaporization to give the corresponding quantities for the vapor at the vapor pressure and  $T_0$ , and finally compute  $h_0^0$  and  $s_0^0$  for the vapor from Equations (22.2) and (22.3). For a gaseous compound we can compute  $(\sum_i \nu_i h_{0i}^0)$  and  $(\sum_i \nu_i s_{0i}^0)$  from Equations (41.8) and (41.10) from equilibrium measurements of a reaction in which the compound is formed from its elements or of some reaction involving the compound with other substances whose constants are known.

When interested only in the effect of pressure on chemical equilibrium at constant temperature, we can use Equation (41.8) with  $K_p^*$  treated as an adjustable parameter.

(44) **Re-examination of the Assumptions of the General Limit Method:** Of the three assumptions made as a basis for the thermodynamic treatment of real gases and gas mixtures, one can be derived as stated earlier from the other two. In particular the assumption regarding the isothermal compressibility of a gas, Equation (13.1), can be derived from the assumption, (13.2), concerning the isothermal variation of the heat content of a pure gas with pressure and that, (26.1), for the ratio of the equilibrium pressure to the partial pressure of a gas in a mixture.

From Equation (13.2) we find for the region of low pressure

$$-T^2 \left[ \frac{\partial(V/T)}{\partial T} \right]_p = \left( \frac{\partial H}{\partial p} \right)_T = B(T, m) + O(p) \quad (T, m \text{ constant}) \quad (44.1)$$

We can write the integral of (44.1) in the form

$$V = T\psi(p, m) + A(T, m) + O(p) \quad (T, m \text{ constant}) \quad (44.2)$$

or

$$pV = T\phi(p, m) + A(T, m)p + O(p^2) \quad (T, m \text{ constant}) \quad (44.3)$$

where (44.3) is in the form of Equation (13.1) except for the first term which is  $F(T, m)$  in (13.1).

The derivations given in Section 27 depend only on the assumption (26.1) for gas mixtures as far as Equation (27.13) which may be written

$$\frac{p_{ek}V}{n_{ek}} \frac{1}{1 + D_i p} - \frac{pV}{(\sum_i n_i) 1 + 2D_m p} \quad (i \equiv k = 1, 2, \dots) \quad (44.4)$$

Consider that  $n_{e1}, n_{e2}, \dots$  moles of the pure gases 1, 2,  $\dots$  and  $(\sum_i n_i)$  moles of the gas mixture are placed in separate compartments each of volume  $V$  and at the temperature  $T$ , and that the chemical potential of each of the pure gases has the same value during all variations as that which it has in the gas mixture. Let the independent variables for each pure gas  $k$  be  $T$  and  $\mu_k$ , and those for the mixture be  $T, \mu_1, \mu_2, \dots$  as in Equations (27.7) and (27.8). Let all variations be in the region of low pressure and at constant temperature and mass. With  $\mu_1$  held constant for both the pure gas 1 and the gas 1 in the mixture, we can vary  $\mu_2, \mu_3, \dots$ , thus causing the pressures and concentrations of the gases 2, 3,  $\dots$  and of the gas mixture to vary. From (27.7) we see that the left-hand side of (44.4) for gas 1 cannot vary except through the factor  $(1 + D_i p)^{-1}$ , but the effect of this variation can be made as small as desired by carrying out all of the variations at sufficiently low pressure. In particular when all variations are carried out at a very low pressure,  $p_{e1}V/n_{e1}$  remains constant, and hence  $pV/(\sum_i n_i)$  for the gas mixture and  $p_{ek}V/n_{ek}$  for each of the other pure gases must have remained constant although  $V, p$ , and  $p_{ek}$  ( $k = 2, 3, \dots$ )

varied. Hence

$$\left(\frac{p_1 V_1}{n_1}\right)^* = \left(\frac{p_2 V_2}{n_2}\right)^* = \dots = \left(\frac{pV}{\sum_i n_i}\right)^* = F(T) \quad (44.5)$$

The subscript  $e$  was omitted since the ratios of (44.5) are each individually constant at constant temperature for the gases and gas mixture each confined in a cylinder.

Thus for any one gas we find

$$(pV)^* = F(T, m) \quad (T, m \text{ constant}) \quad (44.6)$$

for the region of very low pressure. Hence  $T\phi(p, m)$  of Equation (43.3) must equal  $F(T, m)$  and

$$pV = F(T, m) + A(T, m)p + O(p^2) \quad (T, m \text{ constant}) \quad (44.7)$$

which is the assumption (13.1).

#### THE LEWIS AND RANDALL RULE

(45) **The Lewis and Randall Assumption for Gas Mixtures:** Lewis and Randall<sup>1</sup> proposed as a basis for the thermodynamic treatment of gas mixtures the rule: The fugacity  $f_i$  of a gas  $i$  in a mixture is equal to the product of its mole fraction  $x_i$  into the fugacity  $f_{Pk}$  of the pure gas at the total pressure  $p$  and temperature  $T$  of the mixture:

$$f_i = f_{Pk} x_i \quad (i \equiv k = 1, 2, \dots) \quad (45.1)$$

The fugacity  $f$  of a pure gas is defined<sup>2</sup> through the relations

$$\mu = RT \ln f + \psi(T); \quad \lim_{p \rightarrow 0} \frac{f}{p} = 1 \text{ at all temperatures} \quad (45.2)$$

and the fugacity  $f_i$  of a gas  $i$  in a mixture may be defined by the relation

$$\mu_i = RT \ln f_i + \psi_k(T) \quad (i \equiv k = 1, 2, \dots) \quad (45.3)$$

where  $\psi_k(T)$  is the temperature function of Equation (45.2) for the pure gas. Now  $f_i$  is evidently equal to the fugacity of the pure gas  $k$  at its equilibrium pressure  $p_{ek}$  and the temperature of the mixture. According to the Lewis and Randall rule we can write

$$\mu_i = RT \ln f_{Pk} x_i + \psi_k(T) \quad (i \equiv k = 1, 2, \dots) \quad (45.4)$$

The pure gas in the state to which  $f_{Pk}$  refers is, of course, not in equilibrium with the gas mixture since it is under the total pressure of the mixture and not its equilibrium pressure.

<sup>1</sup> G. N. Lewis and M. Randall, *Thermodynamics* (New York: McGraw-Hill Book Co., Inc., 1923), pp. 225-227.

<sup>2</sup> Ref. 1, p. 191.

The Lewis and Randall rule gives immediately the thermodynamic relations of gas mixtures in terms of the independent variables  $p$ ,  $T$ ,  $n_1$ ,  $n_2$ ,  $\dots$ , which are those usually employed in experimental work.

(46) **Deductions from the Lewis and Randall Rule:** The following results may be derived from the rule:

1. Subject to the conditions

$$\begin{aligned} T \text{ (each pure gas)} &= T \text{ (mixture)} \\ p \text{ (each pure gas)} &= p \text{ (mixture)} \\ n_k &= n_i \quad (i \equiv k = 1, 2, \dots) \end{aligned} \quad (\text{B})$$

the following relations hold:

$$\mu_i = \mu_{Pk} + RT \ln x_i \quad (i \equiv k = 1, 2, \dots) \quad (46.1)$$

$$V = (\Sigma_k V_{Pk}) \quad (46.2)$$

$$S = (\Sigma_k S_{Pk}) - (\Sigma_i n_i R \ln x_i) \quad (46.3)$$

$$\left. \begin{aligned} E &= (\Sigma_k E_{Pk}) & H &= (\Sigma_k H_{Pk}) & A &= (\Sigma_k A_{Pk}) + (\Sigma_i n_i RT \ln x_i) \\ F &= (\Sigma_k F_{Pk}) + (\Sigma_i n_i RT \ln x_i) & C_V &= (\Sigma_k C_{V_{Pk}}) & C_p &= (\Sigma_k C_{p_{Pk}}) \end{aligned} \right\} \quad (46.4)$$

where the subscript  $P$  denotes that the conditions (B) apply. Equation (46.2) is Amagat's law.

2. Subject to conditions (B) the partial molar volume of a gas in a mixture equals the molar volume of the pure gas:

$$\left( \frac{\partial V}{\partial n_i} \right)_{pTn} = \frac{V_{Pk}}{n_k} \quad (i \equiv k = 1, 2, \dots) \quad (46.5)$$

3. The Lewis and Randall rule leads to a complete solution of the problem of the determination of the thermodynamic properties of gas mixtures from measurements on pure gases only.

The quantity  $\mu_{Pk}$  can be computed from Equation (45.2) by substitution of  $f_{Pk}$  in the right-hand side. Comparison with Equation (45.4) yields Equation (46.1). Differentiation of Equation (46.1) subject to conditions (B) gives

$$\left( \frac{\partial \mu_i}{\partial p} \right)_{Tn} = \left( \frac{\partial \mu_{Pk}}{\partial p} \right)_T \quad (i \equiv k = 1, 2, \dots) \quad (46.6)$$

$$\left( \frac{\partial \mu_i}{\partial T} \right)_{pn} = \left( \frac{\partial \mu_{Pk}}{\partial T} \right)_p + R \ln x_i \quad (i \equiv k = 1, 2, \dots) \quad (46.7)$$

where the subscript  $n$  denotes constant composition. From general thermodynamic theory the left-hand sides of Equations (46.6) and (46.7) are equal, respectively, to the partial molar volume and the negative partial molar entropy of the gas  $i$  in the mixture, and the partial derivatives on the right-hand

sides are the corresponding molar quantities for the pure gas. Thus

$$\left( \frac{\partial V}{\partial n_i} \right)_{pTn} = \frac{V_{Pk}}{n_k} \quad (i \equiv k = 1, 2, \dots) \quad (46.8)$$

$$\left( \frac{\partial S}{\partial n_i} \right)_{pTn} = \frac{S_{Pk}}{n_k} - R \ln x_i \quad (i \equiv k = 1, 2, \dots) \quad (46.9)$$

The first is Equation (46.5). By Euler's theorem

$$V = \left[ \Sigma_i n_i \left( \frac{\partial V}{\partial n_i} \right)_{pTn} \right] = (\Sigma_k V_{Pk}) \quad (i \equiv k = 1, 2, \dots) \quad (46.10)$$

$$S = \left[ \Sigma_i n_i \left( \frac{\partial S}{\partial n_i} \right)_{pTn} \right] = (\Sigma_k S_{Pk}) - (\Sigma_i n_i R \ln x_i) \quad (i \equiv k = 1, 2, \dots) \quad (46.11)$$

Thus Equations (46.2) and (46.3) are proved. Substitution from Equations (46.1), (46.2), and (46.3) into the general thermodynamic relations (25.4) to (25.9) and use of the conditions (B) give the relations (46.4).

Statement 3 follows directly from the Equations (46.1) through (46.4).

**(47) General Thermodynamic Relations for Gas Mixtures from the Lewis and Randall Rule:** Substitution of the relations for the thermodynamic properties of pure gases derived from the general limit method and given in Section 18 into the Equations (46.1) to (46.4) yields the expressions written below that are derived from the Lewis and Randall rule for gas mixtures.

Equations (47.1) to (47.12) can be expressed in terms of the virial parameters  $\beta_k$ ,  $\gamma_k$ , and  $\delta_k$  of the pure gases through the relations of Section 20; and approximate expressions in terms of the equation of state constants  $A_0$ ,  $B_0$ , and  $c$  through the use of the relations of Section 22.

$$E = \Sigma_k \left\{ \int_0^p \left[ V_k - T \left( \frac{\partial V_k}{\partial T} \right)_{p_k} \right] dp_k - p V_k + n_k h_k^0 \right\} \quad (47.1)$$

$$H = \Sigma_k \left\{ \int_0^p \left[ V_k - T \left( \frac{\partial V_k}{\partial T} \right)_{p_k} \right] dp_k + n_k h_k^0 \right\} \quad (47.2)$$

$$S = \Sigma_k \left\{ \int_0^p \left[ \frac{n_k R}{p_k} - \left( \frac{\partial V_k}{\partial T} \right)_{p_k} \right] dp_k + n_k p_k^0 \right. \\ \left. - (\Sigma_i n_i R \ln p x_i) \right\} \quad (47.3)$$

$$A = \Sigma_k \left\{ \int_0^p \left[ V_k - \frac{n_k R T}{p_k} \right] dp_k - p V_k + n_k (h_k^0 - T s_k^i) \right. \\ \left. + (\Sigma_i n_i R T \ln p x_i) \right\} \quad (47.4)$$

$$F = \Sigma_k \left\{ \int_0^p \left[ V_k - \frac{n_k R T}{p_k} \right] dp_k + n_k (h_k^0 - T s_k) \right. \\ \left. + (\Sigma_i n_i R T \ln p x_i) \right\} \quad (47.5)$$

$$\mu_i = \int_0^p \left[ \frac{V_k}{n_k} - \frac{RT}{p_k} \right] dp_k + RT \ln px_i + h_k^0 - Ts_k^0 \quad (47.6)$$

$$RT \ln f_i = \int_0^p \left[ \frac{V_k}{n_k} - \frac{RT}{p_k} \right] dp_k + RT \ln px_i \quad (47.7)$$

$$C_p = \sum_k \left\{ n_k c_{pk}^* - T \int_0^p \left( \frac{\partial^2 V_k}{\partial T^2} \right)_{p_k} dp_k \right\} \quad (47.8)$$

$$C_V = \sum_k \left\{ n_k c_{pk}^* + n_k R + T \frac{(\partial V_k / \partial T)_{p_k}^2}{(\partial V_k / \partial p_k)_T} - T \int_0^p \left( \frac{\partial^2 V_k}{\partial T^2} \right)_{p_k} dp_k \right\} \quad (47.9)$$

$$C_p - C_V = -T \sum_k \left\{ \frac{(\partial V_k / \partial T)_{p_k}^2}{(\partial V_k / \partial p_k)_T} \right\} \quad (47.10)$$

$$\mu_{J.T.} C_p = T^2 \sum_k \left\{ \left[ \frac{\partial(V_k/T)}{\partial T} \right]_{p_k} \right\} \quad (47.11)$$

$$\eta C_V = - \sum_k \left\{ \frac{T(\partial V_k / \partial T)_{p_k} + p_k (\partial V_k / \partial p_k)_T}{(\partial V_k / \partial p_k)_T} \right\} \quad (47.12)$$

In the foregoing relations the summations extend over all gases in the mixture, and

$$h_k^0 = \int_{T_0}^T c_{pk}^* dT + h_{0k}^0 \quad (47.13)$$

$$\int_{T_0}^T \frac{c_{pk}^*}{T} dT + s_{0k}^0 \quad (47.14)$$

The left-hand sides of Equations (47.1) to (47.5) and (47.8) to (47.12) refer to the gas mixture at  $p$ ,  $T$ , and the mole numbers  $n_i$  ( $i \equiv k = 1, 2, \dots$ ). The terms enclosed in braces are to be computed for each pure gas  $k$  with  $p_k$ ,  $T$ , and  $n_k$  having the values  $p$ ,  $T$ , and  $n_i$  respectively of the mixture, and the sum taken for all gases composing the mixture. The terms not enclosed in braces are to be computed for the gas mixture. In Equations (47.6) and (47.7) the left-hand side refers to a gas in a mixture, and the right-hand side is to be computed for the pure gas as just described except for the term  $px_i$  which refers to the mixture.

(48) **Compressibilities of Gas Mixtures According to the Lewis and Randall Rule:** The Lewis and Randall rule requires Amagat's law to hold at all pressures and temperatures. Thus it places a definite restriction on the equation of state of a gas mixture. Let

$$\frac{V_k}{n_k} = F_k(p, T) \quad (48.1)$$



be the equation of state of a pure gas. The rule gives for the equation of state of a gas mixture

$$V = [\sum_k n_k F_k(p, T)] \quad (48.2)$$

where conditions (B) apply and the summation extends over all species in the mixture. The functions  $F_k(p, T)$  may be different for the different gases, and some or all of the functions may be evaluated graphically. The implications of Equation (48.2) in regard to combination of constants in an equation of state are indicated in Equation (8.8).

**(49) Equilibrium Pressure and Equilibrium Concentration of a Gas in a Mixture:** If we proceed as in Section 36 but use the value of the chemical potential of a gas in a mixture given by the Lewis and Randall rule, Equation (47.6), we find the relations given below for the ratio of the equilibrium pressure  $p_{ek}$  of a gas in a mixture to its partial pressure  $px_i$ . These expressions are to be compared with Equations (36.1) to (36.3). No composition terms appear in the expression given by the Lewis and Randall rule.

Once the equilibrium pressure of a gas has been found, we can compute the corresponding equilibrium concentration from the equation of state (48.1) of the pure gas.

$$RT \ln \frac{p_{ek}}{px_i} = \int_{p_{ek}}^p \left[ \frac{V_k}{n_k} - \frac{RT}{p_k} \right] dp_k \quad (i \equiv k = 1, 2, \dots) \quad (49.1)$$

$$\ln \frac{p_{ek}}{px_i} = \frac{\beta_k}{RT} \left( \frac{p - p_{ek}}{RT} \right) + \frac{\gamma_k}{RT} \left( \frac{p^2 - p_{ek}^2}{2(RT)^2} \right) + \frac{\delta_k}{RT} \left( \frac{p^3 - p_{ek}^3}{3(RT)^3} \right) \quad (49.2)$$

$$\ln \frac{p_{ek}}{px_i} = \left[ B_{0k} - \frac{A_{0k}}{RT} - \frac{c_k}{T^3} \right] \left( \frac{p - p_{ek}}{RT} \right) \quad (49.3)$$

**(50) Effect of an Inert Gas on a Univariant Equilibrium:** In place of the relations (37.7) to (37.9) given by the general limit method, the Lewis and Randall rule leads to the Equations (50.1) to (50.3), given below, for the ratio of the partial pressure  $px_1$  of a vapor 1 to the vapor pressure  $p_{01}$  in a system originally univariant into which an inert gas is introduced. Here  $p_{01}$  is the vapor pressure in the univariant system at the temperature  $T$ , and  $p$  is the total pressure resulting on the addition of an inert gas that is insoluble in the condensed phase or phases. Strictly the application of these equations is limited to the vapor pressure of the pure substance 1 since the integrand refers not to the gas mixture but to substance 1. In their application of the Lewis and Randall rule to the system  $\text{BaCl}_2 \cdot 8\text{NH}_3(s)$ ,  $\text{BaCl}_2(s)$ ,  $\text{NH}_3(g) + \text{N}_2(g)$ , Lurie and Gillespie<sup>1</sup> used the relations only to the vapor pressure of liquid ammonia, with fair results. In other applications<sup>2</sup> of the Lewis and Randall rule the calculations were carried to pressures far above the vapor pressure of the liquid where it is difficult to determine what part of the disagreement is caused by

<sup>1</sup> E. Lurie and L. J. Gillespie, *J. Am. Chem. Soc.*, **49**, 1146 (1927).

<sup>2</sup> M. Randall and B. Sosnick, *J. Am. Chem. Soc.*, **50**, 967 (1928).

failure of the equation of state extrapolation. Gerry<sup>3</sup> found the Lewis and Randall rule extremely bad for cases of condensable vapors at small mole fraction.

The equations given by the Lewis and Randall rule follow.

$$RT \ln \frac{px_1}{p_{01}} = - \int_{p_{01}}^p \left[ \frac{V_1}{n_1} - \frac{RT}{p_1} \right] dp_1 + \int_{p_{01}}^p v_{s1} dp \quad (50.1)$$

$$\ln \frac{px_1}{p_{01}} = \left( v_{s1} - \frac{\beta_1}{RT} \right) \left( \frac{p - p_{01}}{RT} \right) - \left( RT\kappa_1 + \frac{\gamma_1}{RT} \right) \left( \frac{p^2 - p_{01}^2}{2(RT)^2} \right) - \frac{\delta_1}{RT} \left( \frac{p^3 - p_{01}^3}{3(RT)^3} \right) \quad (50.2)$$

$$\ln \frac{px_1}{p_{01}} = \left[ v_{s1} - \left( B_{01} - \frac{A_{01}}{RT} - \frac{c_1}{T^3} \right) \right] \left( \frac{p - p_{01}}{RT} \right) \quad (50.3)$$

(51) **Equilibrium Between Condensed and Gaseous Solutions:** The Lewis and Randall rule has been used extensively for the vapor phase of a multi-component system of two phases: liquid and vapor. These computations were in general for industrial use, and approximations were made for the liquid phase also.

Consider the equilibrium between the liquid and vapor phases of a multi-component system at a total pressure  $p$  and temperature  $T$ . If the liquid were a perfect solution, the fugacity of a substance  $i$  in the liquid phase would be  $f_{iL}y_i$  where  $f_{iL}$  is the fugacity of the pure liquid  $i$  at  $p$  and  $T$ , and  $y_i$  its mole fraction in the solution. The Lewis and Randall rule gives for the fugacity of  $i$  in the vapor  $f_{Pk}x_i$ , where  $f_{Pk}$  is the fugacity of the pure vapor  $i$  at  $p$  and  $T$ , and  $x_i$  its mole fraction in the vapor. At equilibrium

$$f_{iL}y_i = f_{Pk}x_i \quad (i \equiv k = 1, 2, \dots) \quad (51.1)$$

The application of this equation to the design of high-pressure hydrocarbon equipment has been discussed by Brown and his collaborators<sup>1</sup> and by Lewis and Luke<sup>2</sup> who introduced the further approximation that  $f_{iL}$  may be replaced by the fugacity of the pure liquid  $i$  at its own vapor pressure and  $T$ , which is equal to the fugacity of the vapor of  $i$  at the vapor pressure and  $T$ .

In general the evaluation of  $f_{Pk}$  for use in Equation (51.1) requires extrapolation to pressures above the condensation pressure of the pure vapor  $k$ , that is, into the region of supercompressed vapor which has not been investigated experimentally. The extrapolation can be made by use of Equations (18.7)

<sup>3</sup> H. T. Gerry, quoted in L. J. Gillespie, *Chem. Rev.*, **18**, 359 (1936).

<sup>1</sup> C. W. Selheimer, M. Souders, Jr., L. R. Smith, and G. G. Brown, *Ind. Eng. Chem.*, **24**, 515 (1932); M. Souders, Jr., C. W. Selheimer, and G. G. Brown, *ibid.*, **24**, 517 (1932).

<sup>2</sup> W. K. Lewis and C. D. Luke, *Trans. Am. Soc. Mech. Engrs.*, **54**, PME-8, 55 (1932); *Ind. Eng. Chem.*, **25**, 725 (1933).

and (6.3), or from a generalized fugacity chart.<sup>3</sup> The latter involves the use of the law of corresponding states and consists of curves of the ratio  $f/p$  of the fugacity to the pressure of a pure gas plotted against the reduced pressure  $p_r$  for a series of reduced temperatures  $T_r$ . The chart can be prepared from Equation (23.7) and a generalized chart of the compressibility factor, in which  $Z$  is plotted against reduced coordinates.

Although the approximations made in the use of Equation (51.1) are more severe than those of the Lewis and Randall rule, the results are sufficiently accurate for the design of high-pressure hydrocarbon equipment.

We can apply the Lewis and Randall rule to the calculation of equilibrium conditions between a gaseous and a condensed solution, using the argument of Section 40, but evaluating the chemical potential of a gas in a mixture by the rule. The equations for the ratio of the partial pressure  $px_i$  of constituent  $i$  in the vapor phase to the Raoult's law pressure  $p_{0i}y_i$  are given below. They are to be compared with Equations (40.1) to (40.3).

$$RT \ln \frac{px_i}{p_{0i}y_i} = - \int_{p_{0i}}^p \left[ \frac{V_k}{n_k} - \frac{RT}{p_k} \right] dp_k + \int_{p_{0i}}^p v_{si} dp + RT \ln \alpha_i \quad (51.2)$$

( $i \equiv k = 1, 2, \dots$ )

$$\ln \frac{px_i}{p_{0i}y_i} = \left( v_{si} - \frac{\beta_i}{RT} \right) \left( \frac{p - p_{0i}}{RT} \right) - \left( RT\kappa_i + \frac{\gamma_i}{RT} \right) \left( \frac{p^2 - p_{0i}^2}{2(RT)^2} \right) - \frac{\delta_i}{RT} \left( \frac{p^3 - p_{0i}^3}{3(RT)^3} \right) + \ln \alpha_i \quad (51.3)$$

$$\ln \frac{px_i}{p_{0i}y_i} = \left[ v_{si} - \left( B_{0i} - \frac{A_{0i}}{RT} - \frac{c_i}{T^3} \right) \right] \left( \frac{p - p_{0i}}{RT} \right) + \ln \alpha_i \quad (51.4)$$

(52) **Mass Action Function for a Homogeneous Gaseous Reaction:** Applying the general equilibrium relation ( $\sum_i \nu_i \mu_i$ ) to the chemical potential of a gas in a mixture expressed in terms of fugacity, Equation (16.22), we find

$$(\sum_i \nu_i \ln f_i) = \ln K_f = - \frac{1}{RT} [\sum_i \nu_i (h_i^0 - T s_i^0)] = K_p^* \quad (52.1')$$

for the condition of chemical equilibrium. The Lewis and Randall rule gives

$$f_i = f_{Pk} x_i = (f_{Pk}/p)(px_i)$$

where  $px_i$  is the partial pressure of gas  $i$  in the mixture. Thus

$$(\sum_i \nu_i \ln f_i) = \left( \sum_k \nu_k \ln \frac{f_{Pk}}{p} \right) + (\sum_i \nu_i \ln px_i) \quad (52.2)$$

<sup>3</sup> G. G. Brown and collaborators, *Ind. Eng. Chem.*, **24**, 515 (1932); W. K. Lewis, *Ind. Eng. Chem.*, **28**, 257 (1936); R. H. Newton, *Ind. Eng. Chem.*, **27**, 302 (1935).

or

$$\ln \frac{K_p}{K_f} = \ln \frac{K_p}{K_p^*} = - \left( \sum_i \nu_i \ln \frac{f_{Pk}}{p} \right) \quad (52.3)$$

Newton and Dodge<sup>1</sup> used this equation to correlate the data on the ammonia synthesis equilibrium evaluating  $f_{Pk}/p$  from generalized fugacity charts. The agreement between observed and calculated values of  $K_p$  was good at 300 atm, fair at 600 atm, but poor at 1,000 atm.

Another method of deriving the relation for  $K_p$  from the Lewis and Randall rule is to apply the general equilibrium condition to the relation (47.6) given by the rule for the chemical potential of a gas in a mixture. This gives Equation (52.4) first derived by Gillespie.<sup>2</sup> This Equation, (52.6), and (52.7) are to be compared with the general limit relations (41.1), (41.7), and (41.8). The Lewis and Randall relation does not require  $K_p$  to vary with the composition of the equilibrium mixture, as it should, yet the expression does hold to quite high pressures.

The effect of the presence of pure solid phases that take part in the chemical reaction can be included by the method of Section 42.

$$\ln \frac{K_p}{K_p^*} = - \frac{1}{RT} \left\{ \sum_k \nu_k \left[ \int_0^p \left[ \frac{V_k}{n_k} - \frac{RT}{p_k} \right] dp_k \right] \right\} \quad (52.4)$$

$$\ln K_p^* = - \frac{1}{RT} [\sum_i \nu_i (h_i^0 - Ts_i^0)] \quad (52.5)$$

$$\ln \frac{K_p}{K_p^*} = \frac{(\sum_i \nu_i \beta_i)}{RT} \frac{p}{RT} + \frac{(\sum_i \nu_i \gamma_i)}{RT} \frac{p^2}{2(RT)^2} + \frac{(\sum_i \nu_i \delta_i)}{RT} \frac{p^3}{3(RT)^3} \quad (52.6)$$

$$\ln \frac{K_p}{K_p^*} = - \left[ (\sum_i \nu_i \beta_{0i}) - \frac{(\sum_i \nu_i A_{0i})}{RT} - \frac{(\sum_i \nu_i c_i)}{T^3} \right] \frac{p}{RT} \quad (52.7)$$

(53) **Error of the Lewis and Randall Rule:** One of the requirements of the Lewis and Randall rule is that Amagat's law of the additivity of volumes at constant pressure and temperature hold for a gas mixture. This determines how the constants of an equation of state are to be combined to form the corresponding equation for a gas mixture. As indicated in Equation (8.8) we must write

$$\frac{V}{(\sum_i n_i)} = \frac{RT}{p} + \frac{(\sum_i x_i \beta_i)}{RT} + \frac{(\sum_i x_i \gamma_i)}{(RT)^2} p + \frac{(\sum_i x_i \delta_i)}{(RT)^3} p^2 \quad (53.1)$$

that is, linear combination must be employed for each virial parameter. Equation (53.1) may be compared with the relations (9.12) to (9.14) resulting from combination of constants in an equation of state.

<sup>1</sup> R. H. Newton and B. F. Dodge, *J. Am. Chem. Soc.*, **56**, 1287 (1934).

<sup>2</sup> L. J. Gillespie, *J. Am. Chem. Soc.*, **48**, 28 (1926).

Amagat's law and hence the Lewis and Randall rule require that the partial molar volume of a gas in a mixture be equal to the molar volume of the pure gas measured at the total pressure and temperature of the mixture. The error of this as compared with combination of constants in an equation of state is given in Equation (10.6), and is

$$\left(\frac{\partial V}{\partial n_i}\right)_{pTn} - \frac{V_{Pk}}{n_k} = \frac{D_i(\beta)}{RT} + O(p) \quad (i \equiv k = 1, 2, \dots) \quad (53.2)$$

The left-hand side of this equation is the increase in volume of a system consisting of a large quantity of a gas mixture together with a quantity of the pure gas  $k$  at the same pressure and temperature when one mole of substance is removed from the pure gas and combined with the mixture. It was called the expansion of the gas on mixing by Gillespie<sup>1</sup> who studied this property for several different mixtures. In general this quantity is positive except at high pressures and it does not approach zero as the pressure is decreased. Equation (10.3) states the value of  $D_i(\beta)$  in terms of the equation of state constants, temperature, and composition of the mixture.

The error of the Lewis and Randall rule in the computation of fugacity can be determined by comparison of the general limit method relation (31.7) for the fugacity  $f_i$  of a gas in a mixture with the corresponding Lewis and Randall expression  $f_{Pk}x_i$ . The error expressed as a ratio is

$$\ln \frac{f_i}{f_{Pk}x_i} = \frac{1}{RT} \int_0^p \left[ \left(\frac{\partial V}{\partial n_i}\right)_{pTn} - \frac{V_k}{n_k} \right] dp \quad (53.3)$$

Since the integrand of (53.3) is, in general, positive, the fugacity computed from the rule is too small.

The relations for the equilibrium properties of a gas mixture given by the general limit method all contain terms depending on the composition of the mixture which are missing from the equations derived from the Lewis and Randall rule. Thus the general limit method gives for the equilibrium pressure  $p_{ek}$  of a gas in a mixture

$$\ln \frac{p_{ek}}{p x_i} = \frac{\beta_i}{RT} \left( \frac{p - p_{ek}}{RT} \right) + \frac{D_i(\beta)}{RT} \frac{p}{RT} + O(p^2) \quad (53.4)$$

whereas in the Lewis and Randall expression the term containing  $D_i(\beta)$  is missing. Since this is, in general, positive, the equilibrium pressure computed from the rule is too small; or if the equilibrium pressure is given, the corresponding mole fraction  $x_i$  given by the rule is too large.

The results of a number of comparisons of calculations from the Lewis and Randall rule with experiment may be summarized as follows: (1) when all gases in the mixture are far above their critical temperatures, the rule gives good results up to 100 atm and fair results to several hundred atmospheres; (2) when

<sup>1</sup> L. J. Gillespie, *Phys. Rev.*, **34**, 352, 1605 (1929).

one of the gases in the mixture is close to or below its critical point, the rule may fail badly even at moderate pressures; (3) so far as the calculation of the partial molar volume of a gas in a mixture is concerned the absolute error of the rule does not approach zero as the pressure approaches zero, although the fractional error does.

### THE GIBBS-DALTON LAW

(54) **The Gibbs-Dalton Assumption for Gas Mixtures:** As a starting point for the discussion of the thermodynamic properties of gas mixtures, Gibbs<sup>1</sup> proposed the following law: The pressure of a mixture of different gases is equal to the sum of the pressures of the different gases as existing each by itself at the same temperature and with the same value of its (chemical) potential. In commenting on the results derivable from this law Gibbs remarks: "It is in this sense that we should understand the law of Dalton, that every gas is as a vacuum to every other gas."

Gillespie<sup>2</sup> called the foregoing assumption the Gibbs-Dalton law. He pointed out that it contained the essential idea of equilibrium necessary for a general thermodynamic treatment of gas mixtures and derived the various consequences of the law.

The Gibbs-Dalton law leads to relations for the thermodynamic properties of gas mixtures in terms of the independent variables  $V$ ,  $T$ ,  $n_1$ ,  $n_2$ ,  $\dots$  which are those of the great majority of equations of state.

(55) **Deductions from the Gibbs-Dalton Law:** The different gases "existing each by itself at the same temperature and with the same value of its potential" would evidently each be in equilibrium with the gas mixture through a membrane permeable to that gas alone. The pressure of each gas under these conditions is its equilibrium pressure  $p_e$ ; and the Gibbs-Dalton law states that, subject to the conditions

$$\left. \begin{aligned} T \text{ (each pure gas)} &= T \text{ (mixture)} \\ V \text{ (each pure gas)} &= V \text{ (mixture)} \\ \mu_k &= \mu_i \end{aligned} \right\} \quad (i \equiv k = 1, 2, \dots) \quad (C)$$

the pressure  $p$  of the gas mixture is

$$p = (\sum_k p_{ek}) \quad (55.1)$$

The second condition is unnecessary for Equation (55.1) but is required to fix the value of any extensive property of the pure gases.

The results derivable from the Gibbs-Dalton law may be summarized as follows:

1. The concentration of a gas is the same at equilibrium on each side of a membrane permeable to it alone; and under conditions (C) the number of

<sup>1</sup> J. W. Gibbs, *Scientific Papers*, Vol. I (New York: Longmans, Green and Company, 1906), pp. 155-158.

<sup>2</sup> L. J. Gillespie, *Phys. Rev.*, 36, 121 (1930).

moles of each pure gas is the same as in the mixture:

$$C_{ek} = C_i \quad (i \equiv k = 1, 2, \dots) \quad (55.2)$$

$$n_{ek} = n_i \quad (i \equiv k = 1, 2, \dots) \quad (55.3)$$

2. When conditions (C) apply the following quantities are additive:

$$S = (\Sigma_k S_{ek}) \quad (55.4)$$

$$\begin{aligned} E &= (\Sigma_k E_{ek}) & H &= (\Sigma_k H_{ek}) & A &= (\Sigma_k A_{ek}) \\ F &= (\Sigma_k F_{ek}) & C_V &= (\Sigma_k C_{Vek}) & C_p &= (\Sigma_k C_{pek}) \end{aligned} \quad (55.5)$$

3. When conditions (C) apply the following are also true:

$$\left. \begin{aligned} T \text{ (each pure gas)} &= T \text{ (mixture)} \\ V \text{ (each pure gas)} &= V \text{ (mixture)} \\ n_k &= n_i, \text{ that is, } C_k = C_i \quad (i \equiv k = 1, 2, \dots) \end{aligned} \right\} \quad (A)$$

and

$$p = (\Sigma_k p_{ek}) \quad (55.6)$$

$$\mu_i = \mu_{ek} \quad (55.7)$$

$$\begin{aligned} S &= (\Sigma_k S_{ek}) \\ E &= (\Sigma_k E_{ek}) & H &= (\Sigma_k H_{ek}) & A &= (\Sigma_k A_{ek}) \\ F &= (\Sigma_k F_{ek}) & C_V &= (\Sigma_k C_{Vek}) & C_p &= (\Sigma_k C_{pek}) \end{aligned} \quad (55.8)$$

where the subscript *c* denotes that conditions (A) apply. Equation (55.6) is the usual statement of Dalton's law. Although Dalton's law is a consequence of the Gibbs-Dalton law, the converse cannot be proved, since the idea of equilibrium is lacking in Dalton's law.

4. Subject to conditions (A):

$$\left( \frac{\partial p}{\partial n_i} \right)_{VTn} = \left( \frac{\partial p_{ek}}{\partial n_k} \right)_{VT} \quad (i \equiv k = 1, 2, \dots) \quad (55.9)$$

5. The Gibbs-Dalton law leads to a complete solution of the problem of the determination of the thermodynamic properties of gas mixtures from information on the behavior of pure gases only.

Consider a number of systems, one consisting of a gas mixture and each of the others of one of the pure constituent gases. Let the conditions (C) apply for all variations. From Equation (55.1) we find

$$\left( \frac{\partial p}{\partial \mu_i} \right)_{T\mu} = \left( \frac{\partial p_{ek}}{\partial \mu_k} \right)_T \quad (i \equiv k = 1, 2, \dots) \quad (55.10)$$

$$\left( \frac{\partial p}{\partial T} \right)_\mu = \left[ \Sigma_k \left( \frac{\partial p_{ek}}{\partial T} \right)_{\mu k} \right] \quad (55.11)$$

Substitution from the foregoing equations into (27.9) and (27.10) gives

$$\frac{n_i}{V} = \frac{n_{ek}}{V} \quad (i \equiv k \quad 1, 2, \dots) \quad (55.12)$$

$$\frac{S}{V} = \left[ \sum_k \frac{S_{ek}}{V} \right] \quad (55.13)$$

Since  $n/V$  is the concentration  $C$ , Equation (55.2) is proved; and since  $V$  has the same value for the gas mixture and each pure gas, (55.3) and (55.4) are true. To prove the Equations (55.5) we substitute from (55.1), (55.3), and (55.4) into the general thermodynamic relations for pure gases and mixtures, Equations (25.4) to (25.9), making use of conditions (C).

From Equations (55.2) and (55.3) it is evident that the conditions (C) imply the conditions (A), provided the Gibbs-Dalton law is true. Now conditions (A) and (C) each define the same state of each pure gas as regards both intensive and extensive thermodynamic properties. Hence when conditions (A) apply, the chemical potential of each pure gas has the same value as in the mixture, Equation (55.7), and Equations (55.1), (55.4), and (55.5) become (55.6) and (55.8).

Differentiation of Equation (55.6) with respect to  $n_i$  ( $= n_k$ ), ( $i \equiv k = 1, 2, \dots$ ), subject to the conditions (A) gives Equation (55.9).

The relations (55.6) to (55.8) state the properties of a gas mixture in terms of those of the pure constituent gases without requiring any measurements on the mixture.

(56) **General Thermodynamic Relations for Gas Mixtures from the Gibbs-Dalton Law:** In terms of the relations for the thermodynamic properties of pure gases derived by the general limit method and listed in Section 19, the Gibbs-Dalton law yields the relations written below for a gas mixture. They follow immediately from Equations (55.6) to (55.8).

$$E = \sum_k \left\{ \int_V^\infty \left[ p_k - T \left( \frac{\partial p_k}{\partial T} \right)_{V_k} \right] dV_k + n_k e_k^0 \right\} \quad (56.1)$$

$$H = \sum_k \left\{ \int_V^\infty \left[ p_k - T \left( \frac{\partial p_k}{\partial T} \right)_{V_k} \right] dV_k + p_k V + n_k e_k^0 \right\} \quad (56.2)$$

$$S = \sum_k \left\{ \int_V^\infty \left[ \frac{n_k R}{V_k} - \left( \frac{\partial p_k}{\partial T} \right)_{V_k} \right] dV_k + n_k R \ln \frac{V}{n_k R T} + n_k s_k^0 \right\} \quad (56.3)$$

$$A = \sum_k \left\{ \int_V^\infty \left[ p_k - \frac{n_k R T}{V_k} \right] dV_k - n_k R T \ln n_k R T \right. \\ \left. + n_k (e_k^0 - T s_k^0) \right\} \quad (56.4)$$



$$F = \sum_k \left\{ \int_V^\infty \left[ p_k - \frac{n_k RT}{V_k} \right] dV_k - n_k RT \ln \frac{V}{n_k RT} + p_k V + n_k (e_k^0 - T s_k^0) \right\} \quad (56.5)$$

$$\mu_i = \int_V^\infty \left[ \left( \frac{\partial p_k}{\partial n_k} \right)_{V_k T} - \frac{RT}{V_k} \right] dV_k - RT \ln \frac{V}{n_k RT} + RT + (e_k^0 - T s_k^0) \quad (56.6)$$

$$RT \ln f_i = \int_V^\infty \left[ \left( \frac{\partial p_k}{\partial n_k} \right)_{V_k T} - \frac{RT}{V_k} \right] dV_k - RT \ln \frac{V}{n_k RT} \quad (56.7)$$

$$C_p = \sum_k \left\{ n_k c_{pk}^* - n_k R - T \frac{(\partial p_k / \partial T)^2 V_k}{(\partial p_k / \partial V_k)_T} - T \int_V^\infty \left( \frac{\partial^2 p_k}{\partial T^2} \right)_{V_k} dV_k \right\} \quad (56.8)$$

$$C_V = \sum_k \left\{ n_k c_{vk}^* - T \int_V^\infty \left( \frac{\partial^2 p_k}{\partial T^2} \right)_{V_k} dV_k \right\} \quad (56.9)$$

$$C_p - C_V = -T \sum_k \left\{ \frac{(\partial p_k / \partial T)^2 V_k}{(\partial p_k / \partial V_k)_T} \right\} \quad (56.10)$$

$$\mu_{J.T.} C_p = - \sum_k \left\{ \frac{T(\partial p_k / \partial T)_{V_k} + V_k (\partial p_k / \partial V_k)_T}{(\partial p_k / \partial V_k)_T} \right\} \quad (56.11)$$

$$\eta C_V = T^2 \sum_k \left\{ \left[ \frac{\partial (p_k / T)}{\partial T} \right]_{V_k} \right\} \quad (56.12)$$

In these relations the summations extend over all of the gases in the mixture, and:

$$e_k^0 = \int_{T_0}^T c_{vk}^* dT + e_{0k}^0 \quad (56.13)$$

$$\int_{T_0}^T \frac{c_{vk}^*}{T} dT + R \ln \frac{T}{T_0} + S_{0k}^0 \quad (56.14)$$

The quantities  $e_{0k}^0$  and  $S_{0k}^0$  are the molar energy and entropy constants for the pure gas  $k$  at the temperature  $T_0$ , and  $c_{vk}^*$  the molar constant-volume heat capacity at zero pressure.

In each of the Equations (56.1) to (56.5) and (56.8) to (56.12) the left-hand side is the value of a thermodynamic quantity of a gas mixture at  $V$ ,  $T$ , and the mole numbers  $n_i$  ( $i \equiv k = 1, 2, \dots$ ). The terms enclosed in the braces on the right-hand side are to be computed for each pure gas  $k$  with  $V$ ,  $T$ ,  $n_k$ , or  $V$ ,  $T$ ,  $n_k/V$  having the same values for each pure gas as in the gas mixture, and the sum taken for all of the gases composing the mixture. In Equations (56.6) and (56.7) the left-hand side is the value of a quantity for gas  $i$  in the mixture, and the right-hand side is computed for the pure gas as just described.

## (57) Compressibility of Gas Mixtures According to the Gibbs-Dalton Law:

Let

$$p_k = \phi_k(T, n_k/V) \quad (57.1)$$

be the equation of state of a pure gas. The Gibbs-Dalton law gives for the total pressure  $p$  of the gas mixture the relation

$$p = (\sum_k p_k) = [\sum_k \phi_k(T, n_k/V)] \quad (57.2)$$

where the conditions (A) apply and the summation extends over all species in the mixture. Equation (57.2) is Dalton's law as stated in Section 8. The same form of the function  $\phi_k$  need not be used for all of the gases and indeed  $\phi_k$  can be evaluated graphically for some or all of the gases involved.

The error of Dalton's law is discussed in Section 10. The implications of the law in regard to combination of constants in an equation of state are indicated in Equation (8.4).

**(58) Equilibrium Pressure and Equilibrium Concentration of a Gas in a Mixture:** The Gibbs-Dalton law is particularly well suited to the calculation of the equilibrium pressure and concentration of a gas in a mixture.<sup>1</sup>

1. Given the volume  $V$ , temperature  $T$ , and mole numbers  $n_1, n_2, \dots$  of the gas mixture, to find the equilibrium concentrations and pressures of the constituent gases: The equilibrium concentration  $C_{ek}$  of gas  $i$  is simply its concentration  $n_i/V$  in the mixture

$$C_{ek} = C_i \quad (i \equiv k = 1, 2, \dots) \quad (58.1)$$

The equilibrium pressure of each gas at  $T$  and  $C_{ek}$  can now be computed from its equation of state (57.1).

2. Given the total pressure  $p$ , temperature  $T$ , and composition  $x_1, x_2, \dots$  of the gas mixture, to find the equilibrium pressures and concentrations of the individual gases: By successive approximations we can compute the molar volume  $V$  of the mixture from Equation (57.2), which may be written

$$p = \phi_1(T, x_1/V) + \phi_2(T, x_2/V) + \dots \quad (58.2)$$

the desired equilibrium pressures,  $p_{ek} \equiv \phi_k(T, x_k/V)$ , being evaluated at the same time. The equilibrium concentrations are then  $x_k/V$ .

3. Given the total pressure  $p$ , the temperature  $T$ , and the equilibrium pressures  $p_{ek}$  of  $m - 1$  of the  $m$  substances in the gas phase, to calculate the equilibrium concentrations and the composition of the individual gases: Compute the equilibrium pressure of the  $m$ -th substance by difference. From the  $m$  equations of state (57.1) of the pure gases,  $p_{ek} = \phi_k(T, n_k/V)$ , we can compute the equilibrium concentration  $n_k/V (\equiv n_{ek}/V)$  of each gas which is also the

<sup>1</sup> E. Lurie and L. J. Gillespie, *J. Am. Chem. Soc.*, **49**, 1146 (1927); L. J. Gillespie, *Phys. Rev.*, **36**, 121 (1930).

concentration  $n_i/V$  of gas  $k$  in the mixture. Whence

$$x_i = \frac{n_i/V}{[\sum_i (n_i/V)]} \quad (58.3)$$

(59) **Effect of an Inert Gas on a Univariant Equilibrium:** The equilibrium vapor pressure of the substance 1 over the condensed complex is, by Equation (37.4),

$$RT \ln \frac{p_{e1}}{p_{01}} = - \int_{p_{01}}^{p_{e1}} \left[ \frac{V_1}{n_1} - \frac{RT}{p_1} \right] dp_1 + \int_{p_{01}}^{p_{e1}} v_{s1} dp \quad (59.1)$$

This equation depends on the general limit assumptions for pure gases but not on that for gas mixtures, so that  $p_{e1}$  is the true equilibrium vapor pressure of substance 1 over the condensed complex.

The data on the system may be given in either of the two alternate forms considered in sections 2 or 3 of Section 58, and the computation is carried out as outlined there. The equilibrium pressure of substance 1 must satisfy Equation (59.1) if the method of section 2 is used, and is given by Equation (59.1) for the method of section 3.

In some cases the Gibbs-Dalton law may require extrapolation of the equation of state or a plot of  $p$  against  $V$  for a vapor into the region of supersaturation. Since the effect of hydrostatic pressure on vapor pressure is small, the extrapolation is, in general, not severe. In this particular the Gibbs-Dalton law is superior to the Lewis and Randall rule which requires extrapolation to the total pressure of the system.

In their application of the Gibbs-Dalton law to the system  $\text{BaCl}_2 \cdot 8\text{NH}_3(s)$ ,  $\text{BaCl}_2(s)$ ,  $\text{NH}_3(g) + \text{N}_2(g)$ , Lurie and Gillespie computed the equilibrium pressure of ammonia in the gas phase from the known total pressure, temperature, and composition of the mixture. The equilibrium pressure of ammonia so determined should agree with the vapor pressure of the univariant system  $\text{BaCl}_2 \cdot 8\text{NH}_3(s)$ ,  $\text{BaCl}_2(s)$ ,  $\text{NH}_3(g)$  when the solid phases are under a hydrostatic pressure equal to the total gas pressure, as computed from Equation (59.1). The Gibbs-Dalton law gave too high an equilibrium pressure of ammonia, the deviations being in the same direction as those of the ideal gas computation,  $p_{ek} = px_i$ , and up to moderate pressure roughly one half as large. There is an indication that the deviations of the equilibrium pressures computed from the Gibbs-Dalton law may pass through zero and change sign at higher pressures. When the mole fraction of the vapor is very small, as in the system  $\text{I}_2(s)$ ,  $\text{I}_2(g) + \text{N}_2(g)$ , the Gibbs-Dalton law may give no better results than the ideal gas approximation.<sup>1</sup>

(60) **Equilibrium Between Condensed and Gaseous Solutions:** Equation (38.3) is the relation for the chemical potential of a constituent  $i$  of a condensed solution. The chemical potential of a constituent of a gaseous solution is equal to that of the pure gas at its equilibrium pressure  $p_{ek}$  and the temperature of

<sup>1</sup> H. T. Gerry and L. J. Gillespie, *Phys. Rev.*, **40**, 269 (1932).

the mixture, and is given by Equation (18.6) with  $p$  replaced by  $p_{ek}$ . Equating these two expressions, we find at equilibrium

$$RT \ln \frac{p_{ek}}{p_{0i} y_i} = - \int_{p_{0i}}^{p_{ek}} \left[ \frac{V_k}{n_k} - \frac{RT}{p_k} \right] dp_k + \int_{p_{0i}}^p v_{si} dp + RT \ln \alpha_i \quad (i \equiv k = 1, 2, \dots) \quad (60.1)$$

This equation depends on the general limit assumptions for pure gases but not on that for gas mixtures.

The method of application of the Gibbs-Dalton law is similar to that of Section 59, with  $p_{ek}$  given by Equation (60.1).

(61) **Mass Action Function for a Homogeneous Gas Reaction:** Application of the general equilibrium condition ( $\sum_i \nu_i \mu_i$ ) to the relation (56.6) yields immediately a relation for  $K_C$ . To find  $K_p$  we add and subtract a term  $RT \ln p x_i$  before applying the general equilibrium condition. The following relations result.

$$\ln \frac{K_C}{K_C^*} = - \frac{1}{RT} \left\{ \sum_k \nu_k \left[ \int_V^\infty \left[ \left( \frac{\partial p_k}{\partial n_k} \right)_{V, T} - \frac{RT}{V_k} \right] dV_k \right] \right\} \quad (61.1)$$

$$\ln K_C^* = - \frac{1}{RT} \{ \sum_k \nu_k [e_k^0 + RT - Ts_k^0 + RT \ln RT] \} \quad (61.2)$$

$$\begin{aligned} \ln \frac{K_p}{K_p^*} = & - \frac{1}{RT} \left\{ \sum_k \nu_k \left[ \int_V^\infty \left[ \left( \frac{\partial p_k}{\partial n_k} \right)_{V, T} - \frac{RT}{V_k} \right] dV_k \right] \right\} \\ & + (\sum_i \nu_i) \ln \frac{pV}{(\sum_i n_i) RT} \end{aligned} \quad (61.3)$$

$$\ln K_p^* = - \frac{1}{RT} \{ \sum_k \nu_k [e_k^0 + RT - Ts_k^0] \} \quad (61.4)$$

In these equations the terms enclosed in braces are evaluated for each pure gas  $k$  in the mixture, with  $V$ ,  $T$ , and  $n_k/V$  having the same values for each pure gas as in the mixture. The summation extends over all gases in the mixture with  $\nu_k = 0$  for gases that do not take part in the chemical reaction. The last term in Equation (61.3) is to be computed for the gas mixture, the sum  $(\sum_i n_i)$  being taken for all gases in the mixture. It will be noticed that both  $K_C$  and  $K_p$  are functions of the composition of the equilibrium mixture as well as of temperature and volume or pressure.

To compute  $K_C$  for a given chemical reaction at a given molar volume  $V$  and temperature  $T$ : (1) calculate  $K_C^*$  for the given temperature and as a first approximation set  $K_C = K_C^*$  (the ideal gas relation), from which a provisional set of equilibrium mole fractions can be obtained; (2) these mole fractions are the  $n_k$ 's which together with  $V$  and  $T$  permit an approximate evaluation of the right-hand side of Equation (61.1) and hence a second approximation to  $K_C$  and the equilibrium mole fractions. The process can be repeated until no

further change in composition results. The convergence of the calculation to the final equilibrium composition is rapid.

To compute  $K_p$  for a given pressure  $p$  and temperature  $T$  from Equations (61.3) and (61.4) the same method is employed. However, the volume of the mixture must be calculated at each stage of the computation from Equation (57.2).

(62) **Error of the Gibbs-Dalton Law:** The Gibbs-Dalton law requires Dalton's law of the additivity of pressure at constant volume and temperature to hold for a gas mixture. The implications of this as regards the equation of state for mixtures are indicated in Equation (8.4): the  $n$ -th virial parameter  $A_n$  of the mixture is a homogeneous function of the  $n$ -th degree in the mole fractions,  $A_n = (\sum_i x_i^n A_i)$ .

As a result of this the quantity  $(\partial p / \partial n_i)_{VTn}$  for a gas mixture is found to be equal to  $(\partial p_{ek} / \partial n_k)_{VT}$  for each pure gas measured at the temperature and the concentration of that gas in the mixture, Equation (55.9). The experimentally determined compressibilities of gases and gas mixtures have not been studied directly with a view to determining how well this condition is obeyed, as has been done for the partial molar volume and molar volume. If we consider that the equation of state (9.12) to (9.14) for gas mixtures gives a satisfactory representation of these derivatives, the error of the Gibbs-Dalton result is, from Equation (10.9),

$$\begin{aligned} \left( \frac{\partial p}{\partial n_i} \right)_{VTn} - \left( \frac{\partial p_{ek}}{\partial n_k} \right)_{VT} \\ = [\beta_i(1 - 2x_i) + D_i(\beta) + \beta_m] \frac{(\sum_i n_i)}{V^2} + O\left(\frac{1}{V^3}\right) \\ (i \equiv k = 1, 2, \dots) \quad (62.1) \end{aligned}$$

The right-hand side of (62.1) may be either positive, zero, or negative.

The general limit method for gas mixtures gives for the ratio of the equilibrium concentration  $C_{ek}$  of a gas in a mixture to its concentration  $C_i$  in the mixture

$$\begin{aligned} \ln \frac{C_{ek}}{C_i} = [\beta_i + D_i(\beta) + \beta_m] \frac{C}{RT} - 2\beta_i \frac{C_{ek}}{RT} + O(C^2) \\ (i \equiv k = 1, 2, \dots) \quad (62.2) \end{aligned}$$

where  $C$  is the concentration,  $(\sum_i n_i)/V$ , of the mixture. The Gibbs-Dalton law requires that the right-hand side of this expression be zero.

Up to moderate pressures the equilibrium pressure of a gas in a mixture computed from the Gibbs-Dalton law is too large. Since the Lewis and Randall rule gives too small a value for this quantity in the same pressure range, the true value lies somewhere between those given by these two assumptions for gas mixtures.

CORRECTION OF THE INDICATIONS OF A GAS THERMOMETER FOR  
THE IMPERFECTION OF THE GAS

(63) **The Idealized Constant Volume and Constant Pressure Gas Thermometers:**<sup>1</sup> Two types of gas thermometers—constant volume and constant pressure—are in general use for the realization of the absolute temperature scale. In each the experimental instrument differs from the idealized one in important respects and the real thermometric fluid differs from a perfect one.

In the idealized constant volume (or constant density) gas thermometer a definite mass  $N$  of gas is enclosed in a bulb of invariant volume  $V_0$ , the density of the gas being constant throughout the bulb. The pressures  $p_0$ ,  $p_{100}$ , and  $p_t$  of the gas are measured while the bulb is thermostated at the respective temperatures  $0^\circ$ ,  $100^\circ$ ,  $t^\circ\text{C}$ . The mean coefficient  $\alpha_v$  of thermal pressure increase at constant volume of the gas from  $0^\circ$  to  $100^\circ\text{C}$ , and the Centigrade temperature  $t_v$  on the constant volume scale of the gas (corresponding to  $t^\circ\text{C}$ ), each for the gas density corresponding to a pressure of  $p_0$  at  $0^\circ\text{C}$ , are defined by means of the relations

$$p_{100} = p_0(1 + 100\alpha_v) \quad (V \text{ constant}; N = \text{constant}) \quad (63.1)$$

$$p_t = p_0(1 + \alpha_v t_v) \quad (V \text{ constant}; N = \text{constant}) \quad (63.2)$$

where  $\alpha_v$  has the same value in both equations. Equation (63.1) may be written

$$p_{100}V_{100} = p_0V_0(1 + 100\alpha_v) \quad (V_{100} = V_0; N = \text{constant}) \quad (63.3)$$

$$\alpha_v = \frac{p_{100} - p_0}{100p_0} = \frac{p_{100}V_{100} - p_0V_0}{100p_0V_0} \quad (V_{100} = V_0; N = \text{constant}) \quad (63.4)$$

and Equation (63.2) written

$$p_t V_t = p_0 V_0 (1 + \alpha_v t_v) \quad (V_t = V_0; N = \text{constant}) \quad (63.5)$$

$$t_v = \frac{p_t - p_0}{\alpha_v p_0} = \frac{p_t V_t - p_0 V_0}{\alpha_v p_0 V_0} \quad (V_t = V_0; N = \text{constant}) \quad (63.6)$$

$$100 \frac{p_t - p_0}{p_{100} - p_0} = 100 \frac{p_t V_t - p_0 V_0}{p_{100} V_{100} - p_0 V_0} \quad (V_t = V_{100} = V_0; N = \text{constant}) \quad (63.7)$$

There are two forms of idealized constant pressure gas thermometer. In the first a definite mass  $N$  of gas is enclosed in a bulb of variable volume, the pressure being constant throughout the system and having the value  $p_0$ . The volumes  $V_0$ ,  $V_{100}$ , and  $V_t$  of the bulb are measured when the bulb is thermostated at the respective temperatures  $0^\circ$ ,  $100^\circ$ ,  $t^\circ\text{C}$ , the pressure being brought to the value  $p_0$  at each temperature by adjustment of the volume of the bulb.

<sup>1</sup> The following discussion is taken largely from J. A. Beattie, M. Benedict, and J. Kaye, *Proc. Amer. Acad. Arts Sci.*, 74, 343-370 (1941).

The mean coefficient  $\alpha_p$  of thermal dilation at constant pressure of the gas from  $0^\circ$  to  $100^\circ\text{C}$ , and the Centigrade temperature  $t_p$  on the constant pressure scale of the gas (corresponding to  $t^\circ\text{C}$ ), each for the gas pressure  $p_0$ , are defined by means of the relations

$$V_{100} = V_0(1 + 100\alpha_p) \quad (p = \text{constant}; N = \text{constant}) \quad (63.8)$$

$$V_t = V_0(1 + \alpha_p t_p) \quad (p = \text{constant}; N = \text{constant}) \quad (63.9)$$

where  $\alpha_p$  has the same value in both equations. Equation (63.8) may be written

$$p_{100}V_{100} = p_0V_0(1 + 100\alpha_p) \quad (p_{100} = p_0; N = \text{constant}) \quad (63.10)$$

$$\alpha_p = \frac{V_{100} - V_0}{100V_0} = \frac{p_{100}V_{100} - p_0V_0}{100p_0V_0} \quad (p_{100} = p_0; N = \text{constant}) \quad (63.11)$$

and Equation (63.9) written

$$p_t V_t = p_0 V_0(1 + \alpha_p t_p) \quad (p_t = p_0; N = \text{constant}) \quad (63.12)$$

$$\frac{V_t - V_0}{\alpha_p V_0} = \frac{p_t V_t - p_0 V_0}{\alpha_p p_0 V_0} \quad (p_t = p_0; N = \text{constant}) \quad (63.13)$$

$$= 100 \frac{V_t - V_0}{V_{100} - V_0} = 100 \frac{p_t V_t - p_0 V_0}{p_{100} V_{100} - p_0 V_0} \quad (p_t = p_{100} = p_0; N = \text{constant}) \quad (63.14)$$

In the second form of idealized constant pressure thermometer a definite mass  $N$  of gas is enclosed in a bulb of invariant volume  $V_b$  connected by a tube of negligible volume to a pipette of variable volume  $v$  which is kept at a constant temperature (say  $0^\circ\text{C}$ ), the pressure being constant throughout the system and having the value  $p_0$ . The method of operation is the same as that described in the preceding paragraph except that the pressure is adjusted to  $p_0$  at each bulb temperature by adjustment of the volume of gas in the pipette. Let  $v_0$ ,  $v_{100}$ , and  $v_t$  be the gas volumes in the pipette (at  $0^\circ\text{C}$ ) when the bulb temperatures are, respectively,  $0^\circ$ ,  $100^\circ$ ,  $t^\circ\text{C}$ . Then

$$V_b + v_0 = \frac{1}{1 + 100\alpha_p} + v_{100} \quad (p = \text{constant}; N = \text{constant}) \quad (63.15)$$

$$V_b + v_0 = \frac{V_b}{1 + \alpha_p t_p} + v_t \quad (p = \text{constant}; N = \text{constant}) \quad (63.16)$$

where  $\alpha_p$  has the same value in both equations. Thus

$$\alpha_p = \frac{1}{100} \frac{v_{100} - v_0}{V_b - (v_{100} - v_0)} \quad (p = \text{constant}; N = \text{constant}) \quad (63.17)$$

$$t_p = \frac{1}{\alpha_p} \frac{v_t - v_0}{V_b - (v_t - v_0)} \quad (p = \text{constant}; N = \text{constant}) \quad (63.18)$$

Let  $D_0$ ,  $D_{100}$ , and  $D_t$  be the gas densities in the bulb at the respective temperatures  $0^\circ$ ,  $100^\circ$ ,  $t^\circ\text{C}$ . Then

$$N = D_0(V_b + v_0)$$

The number of moles of gas in the bulb at  $100^\circ$  and  $t^\circ\text{C}$  are, respectively,

$$N_{b100} = D_0(V_b + v_0) - D_0v_{100}$$

$$N_{bt} = D_0(V_b + v_0) - D_0v_t$$

and the densities of the gas *in the bulb* at  $100^\circ$  and  $t^\circ\text{C}$  are, respectively,

$$D_{100} = \frac{N_{b100}}{V_b} = D_0 \frac{V_t - (v_{100} - v_0)}{V_b}$$

$$D_t = \frac{N_{bt}}{V_b} = D_0 \frac{V_b - (v_t - v_0)}{V_b}$$

Whence

$$D_0 = D_{100}(1 + 100\alpha_p) \quad (p = \text{constant}) \quad (63.19)$$

$$D_0 = D_t(1 + \alpha_p t_p) \quad (p = \text{constant}) \quad (63.20)$$

where  $\alpha_p$  has the same value in both equations; and

$$\alpha_p = \frac{D_0 - D_{100}}{100D_{100}} \quad (p = \text{constant}) \quad (63.21)$$

$$t_p = \frac{D_0 - D_t}{\alpha_p D_t} \quad (p = \text{constant}) \quad (63.22)$$

In all of the Equations (63.8) to (63.22) each of the quantities  $\alpha_p$  and  $t_p$  has the same numerical value for a given pressure  $p_0$  of a given gas. The practical constant pressure gas thermometer corresponds to the second type of idealized instrument described. Equations (63.8) to (63.14) may however be used, the gas in the pipette being considered as part of the dead space.

In the experimental constant volume or constant pressure gas thermometer the pressure is measured on a manometer (usually mercury) which is outside of the thermostat surrounding the thermometer bulb and is connected to the bulb by a fine capillary. Thus a part of the system is at a temperature different from that of the bulb (or those of the bulb and pipette); furthermore the walls of the system are strained because of changes in pressure and temperature, and the system is in a gravitational field.

The observed quantities must be corrected for: (1) the imperfections of the manometer system; and (2) the deviation of the practical from the idealized thermometer system. When pressures or volumes so corrected are substituted into the relations given above, there result values of  $\alpha_p$ ,  $t_p$ ,  $\alpha_p$ , and  $t_p$  which depend on the kind of gas used and on the density or pressure of the gas at  $0^\circ\text{C}$ , and not on the imperfections of the practical thermometer system.



The general thermodynamic theory of real and perfect gases presented in Section 14 gives the result that for any gas

$$\lim_{p_0 \rightarrow 0} \alpha_v = \lim_{p_0 \rightarrow 0} \alpha_p = \alpha = \frac{1}{T_0} \quad (63.23)$$

and

$$\lim_{p_0 \rightarrow 0} t_v = \lim_{p_0 \rightarrow 0} t_p = t \quad (63.24)$$

In these equations  $\alpha$  is the thermometric coefficient,  $\alpha_v$  or  $\alpha_p$ , of an ideal gas:

$$\frac{p_{100}V_{100} - p_0V_0}{100p_0V_0} \quad (p_{100} = p_0 \text{ or } V_{100} = V_0; N = \text{constant})$$

$$\frac{RT_{100} - RT_0}{100RT_0} = \frac{1}{T_c} \quad (63.25)$$

and is independent of density;  $T_0$  is the Kelvin temperature of the ice point; and  $t$  is thermodynamic temperature on the Centigrade scale, the corresponding Kelvin temperature  $T$  being

$$T = t + T_0 \quad (63.26)$$

The extrapolation to zero ice-point pressure indicated in Equations (63.23) and (63.24) may be accomplished: (1) by determination of the value of the quantity for several different ice-point pressures and extrapolation to zero pressure by graphical or analytic methods; (2) by determination of the value of the quantity for one or more ice-point pressures and correction for the deviation of the properties of the real from those of the ideal gas by means of (a) compressibility data on the gas or (b) values of the Joule (for  $\alpha_v$  and  $t_v$ ) or Joule-Thomson (for  $\alpha_p$  and  $t_p$ ) coefficients for the gas. Since Joule coefficients are difficult to measure, the values of  $\alpha_v$  and  $t_v$  may be corrected to zero ice-point pressure from combined measurements of compressibility and of Joule-Thomson coefficients. Method (1) requires only gas thermometric measurements; method (2) requires in addition auxiliary thermodynamic data on the gas used.

(64) **The Equation of State:** The ice-point pressure of a gas thermometer seldom exceeds 1,000 mm of mercury at 0°C. At these low pressures the virial Equations (3.1) and (3.2) may be written in the closed forms

$$pV = A \left( 1 + \frac{B}{V} + \frac{C}{V^2} \right) \quad (64.1)$$

$$pV = A + Bp + C'p^2 \quad (64.2)$$

where  $V$  is the volume of some fixed amount of gas at the pressure  $p$  and Kelvin temperature  $T$ .

In Section 14 we found that

$$\frac{A}{A_0} = \frac{T}{T_0} \quad 1 + \alpha t \quad (64.3)$$

and, if  $V$  is the volume of one mole of gas,

$$A = RT \quad (64.4)$$

where  $R$  is the universal gas constant,  $T$  the Kelvin or absolute thermodynamic temperature,  $t$  the corresponding Centigrade thermodynamic temperature,  $T_0$  the Kelvin temperature of the ice-point, and  $\alpha$  the thermometric coefficient of an ideal gas.

For the purposes of writing some of the following equations in more condensed form, let us define:

$$\begin{aligned} \Delta(x) &\equiv \begin{vmatrix} 1 & 1 & 1 \\ x_0 T_0 & x_{100} T_{100} & x_t T \\ T_0 & T_{100} & T \end{vmatrix} \\ &= (x_{100} T_{100} - x_0 T_0)t - (x_t T - x_0 T_0)100 \\ &= (x_{100} - x_0)T_{100}t - (x_t - x_0)100T \end{aligned}$$

where  $T$  is Kelvin temperature,  $t = T - T_0$ , and the subscripts 0 and 100 refer to  $0^\circ$  and  $100^\circ\text{C}$ . When the symbol  $\Delta(x)_v$  [or  $\Delta(x)_p$ ] is used,  $t$  is to be replaced by the gas temperature  $t_v$ , [or  $t_p$ ], as defined in Equation (63.6) or (63.13); and  $T$  by  $(T_0 + t_v)$ , [or  $(T_0 + t_p)$ ]. Thus

$$\begin{aligned} \Delta(B) &= (B_{100} - B_0)T_{100}t - (B_t - B_0)100T \\ \Delta(B)_v &= (B_{100} - B_0)T_{100}t_v - (B_t - B_0)100(T_0 + t_v) \\ \Delta(B/T) &= (B_{100} - B_0)t - (B_t - B_0)100 \end{aligned}$$

etc. The values of the virial coefficients  $B$ ,  $C$ ,  $C'$  at any temperature should be independent of the value assigned to the temperature. Actually, since  $A_t$  is computed as  $A_0 T/T_0$ , the values of  $B$ ,  $C$ , and  $C'$  do depend to some extent on the value assigned to  $T$ , which should be on the Kelvin scale.

**(65) Correction of the Indications of the Constant Volume Gas Thermometer for the Imperfection of the Gas from Compressibility Data:** In a constant volume gas thermometer the mass of gas is constant and the volume is constant and has the value  $V_0$ . From the pressure  $p$  at any temperature corrected for the lack of ideality of the thermometric system<sup>1</sup> we can compute  $\alpha_v$  and  $t_v$  from Equation (63.4), (63.6), or (63.7).

<sup>1</sup> For these rather complicated corrections see J. A. Beattie, M. Benedict, B. E. Blaisdell, and J. Kaye, *Proc. Amer. Acad. Arts Sci.*, **77**, 255 (1949).

The following relations may be derived from the equations of state (64.1) and (64.2) and the conditions of constant mass and volume:

$$pV_0 = A + B \frac{A}{A_0} p_0 + \left[ C' + \frac{B}{A} (B - B_0) \right] \frac{A^2}{A_0^2} p_0^2 \quad (65.1)$$

$$= A \left\{ 1 + B \frac{p_0}{A_0} + [C - BB_0] \frac{p_0^2}{A_0^2} \right\} \quad (65.2)$$

$$\frac{p}{p_0} = \frac{A}{A_0} \left\{ 1 + (B - B_0) \frac{p_0}{A_0} + [(C'A - C'_0 A_0) + (B - B_0)^2] \frac{p_0^2}{A_0^2} \right\} \quad (65.3)$$

$$= \frac{A}{A_0} \left\{ 1 + (B - B_0) \frac{p_0}{A_0} + [(C - C_0) - 2B_0(B - B_0)] \frac{p_0^2}{A_0^2} \right\} \quad (65.4)$$

$$\frac{p_0}{p} = \frac{A_0}{A} \left\{ 1 - (B - B_0) \frac{p_0}{A_0} - (C'A - C'_0 A_0) \frac{p_0^2}{A_0^2} \right\} \quad (65.5)$$

$$= \frac{A_0}{A} \left\{ 1 - (B - B_0) \frac{p_0}{A_0} - [(C - C_0) - (B^2 - B_0^2)] \frac{p_0^2}{A_0^2} \right\} \quad (65.6)$$

Substitution of the values of  $pV_0$  from Equations (65.1) and (65.2) into Equation (63.4) yields

$$\alpha = \alpha_v - \frac{1 + 100\alpha \frac{B_{100} - B_0}{A_0}}{100} p_0 \times \left\{ 1 + \left[ \frac{C'_{100}(1 + 100\alpha) - C'_0}{B_{100} - B_0} + \frac{B_{100} - B_0}{A_0} \right] p_0 \right\} \quad (65.7)$$

$$= \alpha_v - \frac{1 + 100\alpha \frac{B_{100} - B_0}{A_0}}{100} p_0 \left\{ 1 + \left[ \frac{C_{100} - C_0}{B_{100} - B_0} - 2B_0 \right] \frac{p_0}{A_0} \right\} \quad (65.8)$$

Substitution of the values of  $pV_0$  into Equation (63.7) yields

$$t = t_v + \frac{\Delta(B)}{100A_0} p_0 \left\{ 1 + \left[ \frac{100A_0 \Delta(C'T)}{T_0 \Delta(B)} + 100 \frac{\Delta(B^2)}{\Delta(B)} - (B_{100} + B_0)T_{100} + 2B_0T_0 \right] \frac{p_0}{100A_0} \right\} \quad (65.9)$$

$$= t_v + \frac{\Delta(B)}{100A_0} p_0 \times \left\{ 1 + \left[ 100 \frac{\Delta(C)}{\Delta(B)} - (B_{100} + B_0)T_{100} + 2B_0T_0 \right] \frac{p_0}{100A_0} \right\} \quad (65.10)$$

Equations (65.7) to (65.10) may be written

$$\alpha = \alpha_v - \frac{1 + 100\alpha_v B_{100} - B_0}{100 A_0} p_0 \left\{ 1 + \frac{C'_{100}(1 + 100\alpha_v) - C'_0}{B_{100} - B_0} p_0 \right\} \quad (65.11)$$

$$\begin{aligned} & \frac{1 + 100\alpha_v B_{100} - B_0}{100 A_0} p_0 \\ & \times \left\{ 1 + \left[ \frac{C_{100} - C_0}{B_{100} - B_0} - (B_{100} + B_0) \right] \frac{p_0}{A_0} \right\} \quad (65.12) \end{aligned}$$

$$t = t_v + \frac{\Delta(B)_v}{100A_0} p_0 \left\{ 1 + \left[ \frac{A_0 \Delta(C'T)_v}{T_0 \Delta(B)_v} + \frac{\Delta(B^2)_v}{\Delta(B)} - (B_t + B_0) \right] \frac{p_0}{A_0} \right\} \quad (65.13)$$

$$t_v + \frac{\Delta(B)_v}{100A_0} p_0 \left\{ 1 + \left[ \frac{\Delta(C)_v}{\Delta(B)} - (B_t + B_0) \right] \frac{p_0}{A_0} \right\} \quad (65.14)$$

At the present time the accuracy of gas thermometric measurements is not sufficient to warrant use of the terms of the order of  $p_0^2$ . Thus we may write

$$\alpha_v - F_v p_0 \quad (65.15)$$

$$F_v = \frac{(1 + 100\alpha)(B_{100} - B_0)}{(100RT_0)} \quad (65.16)$$

$$t = t_v + E_v p_0 \quad (65.17)$$

$$E_v = \frac{[t(T_0 + 100)(B_{100} - B_0) - 100(T_0 + t)(B_t - B_0)]}{(100RT_0)} \quad (65.18)$$

(66) **Corrections of the Indications of the Constant Pressure Gas Thermometer for the Imperfection of the Gas from Compressibility Data:** In the constant pressure thermometer the mass of gas is constant and the pressure is constant and has the value  $p_0$ . From the volume  $V$  at any temperature corrected for the lack of ideality of the thermometer system we can compute  $\alpha_p$  and  $t_p$  from Equation (63.11), (63.13), or (63.14).

The following relations can be obtained from the equations of state (64.1) and (64.2) and the conditions of constant mass and pressure:

$$p_0 V = A + B p_0 + C' p_0^2 \quad (66.1)$$

$$= A \left[ 1 + B \frac{p_0}{A} + (C - B^2) \frac{p_0^2}{A^2} \right] \quad (66.2)$$

$$\begin{aligned} \frac{V}{V_0} = \frac{A}{A_0} \left\{ 1 + \left( \frac{B}{A} - \frac{B_0}{A_0} \right) p_0 \right. \\ \left. + \left[ \left( \frac{C'}{A} - \frac{C'_0}{A_0} \right) - \frac{B_0}{A_0} \left( \frac{B}{A} - \frac{B_0}{A_0} \right) \right] p_0^2 \right\} \quad (66.3) \end{aligned}$$

$$= \frac{A}{A_0} \left\{ 1 + \left( \frac{B}{A} - \frac{B_0}{A_0} \right) p_0 + \left[ \left( \frac{C}{A^2} - \frac{C_0}{A_0^2} \right) - \left( \frac{B^2}{A^2} + \frac{BB_0}{AA_0} - \frac{2B_0^2}{A_0^2} \right) \right] p_0^2 \right\} \quad (66.4)$$

$$\frac{V_0}{V} = \frac{A_0}{A} \left\{ 1 - \left( \frac{B}{A} - \frac{B_0}{A_0} \right) p_0 - \left[ \left( \frac{C'}{A} - \frac{C'_0}{A_0} \right) - \frac{B}{A} \left( \frac{B}{A} - \frac{B_0}{A_0} \right) \right] p_0^2 \right\} \quad (66.5)$$

$$= \frac{A_0}{A} \left\{ 1 - \left( \frac{B}{A} - \frac{B_0}{A_0} \right) p_0 - \left[ \left( \frac{C}{A^2} - \frac{C_0}{A_0^2} \right) - \left( \frac{2B^2}{A^2} - \frac{BB_0}{AA_0} - \frac{B_0^2}{A_0^2} \right) \right] p_0^2 \right\} \quad (66.6)$$

Substitution of the values of  $p_0V$  from Equations (66.1) and (66.2) into Equation (63.11) yields

$$\alpha = \alpha_p - \frac{B_{100} - B_0(1 + 100\alpha)}{100A_0} p_0 \times \left\{ 1 + \left[ \frac{C'_{100} - C'_0(1 + 100\alpha)}{B_{100} - B_0(1 + 100\alpha)} - \frac{B_0}{A_0} \right] p_0 \right\} \quad (66.7)$$

$$= \alpha_p - \frac{B_{100} - B_0(1 + 100\alpha)}{100A_0} p_0 \left\{ 1 + \left[ \frac{C_{100} - C_0(1 + 100\alpha)^2}{B_{100} - B_0(1 + 100\alpha)} - B_{100} - 2B_0(1 + 100\alpha) \right] \frac{p_0}{A_0(1 + 100\alpha)} \right\} \quad (66.8)$$

Substitution of the values of  $p_0V$  into Equation (63.14) gives

$$t = t_p + \frac{T_0\Delta(B/T)}{100A_0} p_0 \times \left\{ 1 + \left[ 100A_0 \frac{\Delta(C'/T)}{\Delta(B/T)} - T_0(B_{100} - B_0) \right] \frac{p_0}{100A_0} \right\} \quad (66.9)$$

$$t_p + \frac{T_0\Delta(B/T)}{100A_0} p_0 \left\{ 1 + \left[ 100 \frac{\Delta(C/T^2)}{\Delta(B/T)} - 100 \frac{\Delta(B^2/T^2)}{\Delta(B/T)} - (B_{100} - B_0) \right] \frac{T_0 p_0}{100A_0} \right\} \quad (66.10)$$

Equations (66.7) to (66.11) may be written

$$= \alpha_p - \frac{B_{100} - B_0(1 + 100\alpha_p)}{100A_0} p_0 \left\{ 1 + \frac{C'_{100} - C'_0(1 + 100\alpha_p)}{B_{100} - B_0(1 + 100\alpha_p)} p_0 \right\} \quad (66.11)$$

$$\alpha_p - \frac{B_{100} - B_0(1 + 100\alpha_p)}{100A_0} p_0 \left\{ 1 + \left[ \frac{C_{100} - C_0(1 + 100\alpha_p)^2}{B_{100} - B_0(1 + 100\alpha_p)} - B_{100} - B_0(1 + 100\alpha_p) \right] \frac{p_0}{A_0(1 + 100\alpha_p)} \right\} \quad (66.12)$$

$$t = t_p + \frac{T_0 \Delta(B/T)_p}{100A_0} p_0 \left\{ 1 + \frac{\Delta(C'/T)_p}{\Delta(B/T)_p} p_0 \right\} \quad (66.13)$$

$$= t_p + \frac{T_0 \Delta(B/T)_p}{100A_0} p_0 \left\{ 1 + \left[ \frac{\Delta(C/T^2)_p}{\Delta(B/T)_p} - \frac{\Delta(B^2/T^2)_p}{\Delta(B/T)_p} \right] \frac{T_0 p_0}{A_0} \right\} \quad (66.14)$$

To terms of the order of  $p_0$  we find

$$\alpha = \alpha_p - F_p p_0 \quad (66.15)$$

$$F_p = \frac{[B_{100} - B_0(1 + 100\alpha)]}{(100RT_0)} \quad (66.16)$$

$$t = t_p + E_p p_0 \quad (66.17)$$

$$E_p = \frac{[t(B_{100} - B_0) - 100(B_t - B_0)]}{(100R)} \quad (66.18)$$

(67) **Correction of the Indications of Gas Thermometers for the Imperfection of the Gas from Joule and Joule-Thomson Coefficients:** Let  $\eta$  be the Joule coefficient and  $\mu_{J.T.}$  the Joule-Thomson coefficient of a gas as defined in Section 3. Then  $\lambda$ ,

$$\lambda \equiv \eta C_V \quad (67.1)$$

can be used to correct  $\alpha_v$  and  $t_v$  given by a constant volume gas thermometer for the deviation of the thermometric gas from an ideal gas; and  $\sigma$ ,

$$\mu_{J.T.} C_p \quad (67.2)$$

can be used to correct  $\alpha_p$  and  $t_p$  given by a constant pressure gas thermometer.

For the constant volume gas thermometer we start with the relation

$$\eta C_V \left( \frac{\partial E}{\partial V} \right)_T = T \left( \frac{\partial p}{\partial T} \right)_V - p \equiv - \left[ \frac{\partial(p/T)}{\partial(1/T)} \right]_V \quad (67.3)$$

Thus

$$d \left( \frac{p}{T} \right) = - \lambda d \left( \frac{1}{T} \right) \quad (V = \text{constant}) \quad (67.4)$$

and integration from  $0^\circ$  to  $100^\circ\text{C}$  at constant volume gives

$$\frac{p_{100}}{T_{100}} - \frac{p_0}{T_0} = - \int_{T_0}^{T_{100}} \lambda d\left(\frac{1}{T}\right) \quad (V = V_0 = \text{constant}) \quad (67.5)$$

the integral being evaluated along the constant volume (or density) curve to which  $\alpha_v$  refers (the density of the gas at  $p_0$  and  $T_0$ ). Substitution of the value of  $p_{100}$  obtained from Equation (67.5) into Equation (63.4) and use of (63.25) give

$$\alpha = \alpha_v + \frac{1 + 100\alpha}{100\alpha p_0} \int_{T_0}^{T_{100}} \lambda d\left(\frac{1}{T}\right) \quad (67.6)$$

where  $p_0$  and  $\lambda$  are to be expressed in the same units. In the first approximation the quantity  $\alpha$  on the right hand side of the equation can be replaced by  $\alpha_v$  or by the approximate value  $\alpha = 0.003661$ ,  $T_0$  taken to be  $273.16$ , and  $\lambda$  expressed as a function of  $(T_0 + t_v)$ .

Integration of Equation (67.4) from  $0^\circ$  to  $t^\circ\text{C}$  gives

$$\frac{p_t}{T} - \frac{p_0}{T_0} = - \int_{T_0}^T \lambda d\left(\frac{1}{T}\right) \quad (V = V_0 = \text{constant}) \quad (67.7)$$

Substitution of the value of  $p_t$  from Equation (67.7) and  $p_{100}$  from (67.5) into Equation (63.7) gives

$$t = t_v + \frac{T_0}{100p_0} \left[ 100T \int_{T_0}^T \lambda d\left(\frac{1}{T}\right) - t_v T_{100} \int_{T_0}^{T_{100}} \lambda d\left(\frac{1}{T}\right) \right] \quad (67.8)$$

In the first approximation  $T$  can be replaced by  $(T_0 + t_v)$ ,  $T_0$  taken to be  $273.16$ , and  $\lambda$  expressed as a function of  $(T_0 + t_v)$ .

It will be noted that  $\lambda$  can be computed from the equation of state through Equation (67.3). Thus from Equation (64.1) we find

$$\lambda = \frac{AT}{V^2} \left[ \left( \frac{dB}{dT} \right) + \frac{1}{V} \left( \frac{dC}{dT} \right) \right] \quad (67.9)$$

$$= - \frac{R}{V^2} \left[ \frac{dB}{d(1/T)} + \frac{1}{V} \frac{dC}{d(1/T)} \right] \quad (67.10)$$

For the constant pressure thermometer we start with the relation

$$\sigma \quad \mu_{J.T.C_p} = - \left( \frac{\partial H}{\partial p} \right)_T = T \left( \frac{\partial V}{\partial T} \right)_p - V \equiv - \left[ \frac{\partial(V/T)}{\partial(1/T)} \right]_p \quad (67.11)$$

Thus

$$d\left(\frac{V}{T}\right) = - \sigma d\left(\frac{1}{T}\right) \quad (p = \text{constant}) \quad (67.12)$$

and integration from  $0^\circ$  to  $100^\circ\text{C}$  at constant pressure gives

$$\frac{V_{100}}{T_{100}} - \frac{V_0}{T_0} = - \int_{T_0}^{T_{100}} \sigma d\left(\frac{1}{T}\right) \quad (p = p_0 = \text{constant}) \quad (67.13)$$

the integral being evaluated along the constant pressure curve,  $p_0$ , to which  $\alpha_p$  refers. Substitution of the value of  $V_{100}$  from Equation (67.13) into Equation (63.11) and use of the relation (63.25) give:

$$\alpha_p + \frac{1 + 100\alpha}{100\alpha V_0} \int_{T_0}^{T_{100}} \sigma d\left(\frac{1}{T}\right) \quad (67.14)$$

The quantity  $V_0$  may be computed from  $p_0$  and  $T_0$  by Equation (64.2), and is to be expressed in the same units as  $\sigma$ . The same approximations may be made as for Equation (67.6).

Integration of Equation (67.12) from  $0^\circ$  to  $t^\circ\text{C}$  gives

$$\frac{V_t}{T} - \frac{V_0}{T_0} = - \int_{T_0}^T \sigma d\left(\frac{1}{T}\right) \quad (p = p_0 \text{ constant}) \quad (67.15)$$

Substitution of the value of  $V_t$  from Equation (67.15) and  $V_{100}$  from (67.13) into Equation (63.14) gives

$$t = t_p + 100V_i \left[ 100T \int_{T_0}^T \sigma d\left(\frac{1}{T}\right) - t_p T_{100} \int_{T_0}^{T_{100}} \sigma d\left(\frac{1}{T}\right) \right] \quad (67.16)$$

The same approximations may be made as for Equation (67.8).

From Equation (67.11) and the equation of state (64.2) we find

$$\left( T \frac{dB}{dT} - B \right) + \left( T \frac{dC'}{dT} - C' \right) p \quad (67.17)$$

$$= - \left( \frac{d(B/T)}{d(1/T)} + \frac{d(C'/T)}{d(1/T)} p \right) \quad (67.18)$$

(68) **Values of the Corrections for the Helium, Hydrogen, and Nitrogen Gas Thermometers:** Roebuck and Murrell<sup>1</sup> have employed measured values of  $\sigma$  defined by Equation (67.2) to compute the corrections to the indications of constant pressure gas thermometers; and values of  $\lambda$ , Equation (67.1), computed from  $\sigma$  and compressibility data by Equation (3.12) to compute corrections for constant volume gas thermometers.

Keyes<sup>2</sup> correlated all of the data on the second virial coefficient  $B$  of helium, hydrogen, and nitrogen as determined from compressibility measurements

<sup>1</sup> J. R. Roebuck and T. A. Murrell, *Temperature* (New York: Reinhold Publishing Corporation, 1941), p. 60.

<sup>2</sup> F. G. Keyes, *Temperature*, p. 45.



together with values of the second virial coefficients computed from Joule-Thomson coefficients and constant-pressure heat capacities by the method outlined in Section 2. As a starting point for  $B$  in this latter computation he took  $B$  to be zero at infinite temperature, which seems indicated by Figure 5.

These values of the second virial coefficients give when used in Equations (65.16) and (66.16) the quantities  $F_v$  and  $F_p$  listed in Table IV,<sup>3</sup> and when

TABLE IV  
VALUES OF  $F_v$  AND  $F_p$

Gas	$10^7 F_v$	$10^7 F_p$
	°K <sup>-1</sup> -meter Hg <sup>-1</sup>	
He.....	- 2.2	- 26.8
H <sub>2</sub> .....	+ 12.8	- 20.1
N <sub>2</sub> .....	+132.1	+118.2

substituted into Equations (65.18) and (66.18) the quantities  $E_v$  and  $E_p$  listed in Table V. The former are  $\alpha$  (gas) -  $\alpha$  (ideal gas) in °K<sup>-1</sup> and the latter are  $t$  (thermodynamic) -  $t$  (gas) in Centigrade degrees each for a gas thermometer at an ice-point pressure of one meter of mercury.

TABLE V  
VALUES OF  $E_v$  AND  $E_p$

$t$ °C	$10^4 E_v$			$10^4 E_p$
	°C-meter Hg <sup>-1</sup>			°C-meter Hg <sup>-1</sup>
	Helium	Hydrogen	Nitrogen	Nitrogen
600			2,508	
500			1,809	7,472
400			1,174	5,192
300			660	3,082
200	35	71	250	1,393
- 50	17	37	174	
-100	49	108	616	
-150	101	230	1,879	
-200	181	436		
-250	305	880		
-260	338			
-270	364			

<sup>3</sup> J. A. Beattie, *Temperature*, p. 74.

## INTERMOLECULAR FORCES

(69) **Introduction:** The remainder of this chapter is concerned with the kinetic-molecular theory of the equation of state. It is necessary to consider first the nature of the forces acting between molecules, and the equations describing them.

With the successful application of quantum mechanics to atomic and molecular problems, it has become clear that the important forces are fundamentally electrostatic. The potential energy of a system of molecules may thus be written down at once from Coulomb's law when the positions of all the electrons and nuclei are specified. Use of this potential energy in the Schrödinger wave equation then allows in principle the evaluation of the eigenfunctions and energy levels of the system, from which its macroscopic equilibrium properties can be predicted. Embarking on this procedure, we recall immediately the great disparity in mass between nuclei and electrons, in consequence of which the latter move much more rapidly, executing many cycles of their motion during the time required for the nuclei to move appreciably. To a very good approximation,<sup>1</sup> therefore, the motions of electrons and nuclei can be treated separately. Solution of a Schrödinger equation with the nuclei held in fixed positions, and only the electrons in motion, leads to a set of electronic states for the particular nuclear configuration chosen; with rare exceptions, only the lowest of these is of interest for the present problem, the excited states being but sparsely populated at ordinary temperatures. The energy obtained for this ground electronic state varies with the positions given the nuclei, and constitutes the effective potential energy governing the nuclear motion.<sup>2</sup> It is this quantity which is usually termed the intermolecular potential energy, insofar as it concerns the relative motions of the nuclei in different molecules; and its derivatives with respect to the relative coordinates of the nuclei in different molecules are what we customarily mean by the term *intermolecular forces*. The motion of the molecules under the influence of these forces is then to be determined by solving the Schrödinger equation for the nuclear motion, but for the treatment of gases the laws of classical mechanics will frequently furnish a sufficient approximation to this part of the problem.

We begin our discussion of the intermolecular forces<sup>3</sup> by considering the interaction of a single pair of molecules, first at large and then at smaller distances of separation from each other. Let the individual electrons and nuclei of a molecule be point charges  $e_i$ , located at vector distances  $\mathbf{r}_i$  from its center of mass. According to Coulomb's law, the electrostatic potential  $\phi$  at a point

<sup>1</sup> M. Born and J. R. Oppenheimer, *Ann. Physik*, **84**, 457 (1927).

<sup>2</sup> See, for example, L. Pauling and E. B. Wilson, Jr., *Introduction to Quantum Mechanics* (McGraw-Hill, 1935), Chap. X, for a more complete discussion, particularly with respect to intramolecular motions of nuclei.

<sup>3</sup> For more detailed general discussions of the intermolecular forces consult F. London, *Trans. Faraday Soc.*, **33**, 8 (1937); H. Margenau, *Rev. Mod. Phys.*, **11**, 1 (1939). The latter is a comprehensive review of the long-range forces.

$\mathbf{R}$  is given by  $\phi = \sum_i e_i / |\mathbf{R} - \mathbf{r}_i|$ . If  $\mathbf{R}$  is large compared to all the  $\mathbf{r}_i$ , an expansion gives

$$\phi(\mathbf{R}) = \frac{\sum e_i}{R} + \frac{\sum e_i r_i \cos \theta_i}{R^2} + \frac{\sum e_i r_i^2 (3 \cos^2 \theta_i - 1)}{2R^3} + \dots \quad (69.1)$$

where  $R$  and  $r_i$  are the magnitudes of  $\mathbf{R}$  and  $\mathbf{r}_i$ , and  $\theta_i$  is the angle between  $\mathbf{r}_i$  and  $\mathbf{R}$ . If the molecule is uncharged, the first term vanishes. The second term depends on the *dipole moment*  $\mathbf{u} = \sum e_i \mathbf{r}_i$  of the molecule, and the third on its *quadrupole moment*, whose components, such as  $\sum e_i x_i^2$ , identify it as an electrical moment of inertia. The contributions of still higher-order poles are of little interest, for when they become appreciable it is generally easier to use the unexpanded form of the potential. To find the potential energy  $u$  between this molecule and a second one located at  $\mathbf{R}$ , we must sum the interaction of the potential  $\phi$  with all the charges  $e_j$  of the second molecule, which are located at vector distances  $\mathbf{\rho}_j$  from its center of mass at  $\mathbf{R}$ . For uncharged molecules, with the retention of the dipole terms only, this finally gives

$$u = -\frac{1}{R^3} \sum_{ij} e_i e_j (2z_i \zeta_j - x_i \xi_j - y_i \eta_j) + \dots \quad (69.2)$$

where  $(x_i, y_i, z_i)$  and  $(\xi_j, \eta_j, \zeta_j)$  are the components of  $\mathbf{r}_i$  and  $\mathbf{\rho}_j$ , so chosen that  $z_i$  and  $\zeta_j$  are along  $\mathbf{R}$ . This expression for  $u$ , when averaged over the motions of the electrons, as described above, yields the most important part of the intermolecular potential energy for two widely separated molecules, which is thus due to the interaction of their dipole moments. In all cases, the forces between two molecules at large distances (for asymmetric molecules, after averaging over all relative orientations) are attractive, and are frequently called *van der Waals forces*.

#### (70) Electrostatic Forces; Orientation Effect Between Polar Molecules:

The electronic charge distribution of a rare gas atom in its ground state is spherically symmetrical about the nucleus. The dipole moment of the atom therefore vanishes when it is averaged over all phases of the electronic motion. The same is true of many diatomic and polyatomic molecules (e.g.,  $\text{H}_2$ ,  $\text{N}_2$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_6\text{H}_6$ , etc.), and these constitute the class of *non-polar* molecules. The forces between two such molecules, according to Equation (69.2), will then be negligible<sup>1</sup> unless the electronic motions within one of them are influenced by the presence of the other; this influence is in fact appreciable, and is discussed in Sections 71 and 72.

*Polar* molecules (e.g.,  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{HCl}$ ,  $\text{SO}_2$ , etc.) are those possessing non-vanishing ("permanent") dipole moments  $\mu$  even after averaging over the electronic motion. For two such molecules with permanent moments of mag-

<sup>1</sup> Non-polar molecules often possess permanent quadrupole moments, but it turns out that the forces due to these or higher moments are rarely of primary significance.

nitude  $\mu_1 = \langle \Sigma \epsilon_i \mathbf{r}_i \rangle_{Av}$  and  $\mu_2 = \langle \Sigma \epsilon_i \mathbf{r}_i \rangle_{Av}$ , Equation (69.2) yields a contribution even when the effects of one molecule on the electron-cloud of the other are ignored. This term is readily seen to be

$$\begin{aligned} u &= -(\mu_1 \mu_2 / R^3) (2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos \varphi_1 \cos \varphi_2 \\ &\quad - \sin \theta_1 \sin \theta_2 \sin \varphi_1 \sin \varphi_2) \\ &= -(\mu_1 \mu_2 / R^3) [2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos (\varphi_2 - \varphi_1)] \end{aligned} \quad (70.1)$$

where  $\theta_1$ ,  $\varphi_1$  and  $\theta_2$ ,  $\varphi_2$  are the polar coordinates ("latitude" and "longitude") specifying the orientations of the two dipole moments with respect to the intermolecular axis  $\mathbf{R}$ .

The potential energy of Equation (70.1) is attractive (negative) for some orientations, and repulsive for others. Its unbiased mean over all orientations of either molecule vanishes:

$$\int_0^\pi \int_0^{2\pi} [2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos (\varphi_2 - \varphi_1)] \sin \theta_1 d\theta_1 d\varphi_1 = 0 \quad (70.2)$$

In a gas at equilibrium, however, all orientations are not equally frequent, and the significant average value must be found by including the Boltzmann factor  $e^{-u/kT}$ . When such a weighted average of Equation (70.1) is taken over all orientations of both molecules, the result<sup>2</sup> is

$$\begin{aligned} \langle u e^{-u/kT} \rangle_{Av} &= - \langle u^2 \rangle_{Av} / kT + \dots \\ &= - 2\mu_1^2 \mu_2^2 / 3kTR^6 + \dots \end{aligned} \quad (70.3)$$

showing that the attractive orientations predominate. Kinetically, the net attractive effect results because a molecule which loses kinetic energy at a collision may thereby be "trapped" in an attractive orientation with respect to another molecule, and must then undergo only oscillatory motions until freed by another collision; such trapping is of course not possible for repulsive orientations. If the dipole moments are sufficiently large, such a trapped molecular pair may have sufficient stability to survive a number of collisions, and in such cases it becomes meaningful to consider the phenomenon as a dimerization; this is more fully considered in Section 84.

Application of Equation (70.1), and of corresponding expressions for interactions between permanent quadrupoles, to the equation of state of gases was made by Keesom,<sup>3</sup> following earlier suggestions by Reinganum.<sup>4</sup> These electrostatic forces are consequently sometimes called the Keesom orientation effect, or alignment effect. For the non-polar gases, Keesom evaluated the permanent quadrupole moments necessary to reproduce the observed equation of state, on

<sup>2</sup> The averaging process used here is classical, i.e., integration over all angles. The quantum-mechanical average is found in a different way, but for most cases the classical result will be adequate. See H. Margenau, *loc. cit.*, or J. G. Kirkwood, *J. Chem. Phys.*, **1**, 597 (1933).

<sup>3</sup> W. H. Keesom, *Physik. Z.*, **22**, 129 (1921).

<sup>4</sup> M. Reinganum, *Ann. Physik*, **10**, 334 (1903); **38**, 649 (1912).

the supposition that these accounted for all of the attractive forces, while for the polar gases it was also necessary to supplement the known dipole moments by quadrupoles in order to reach agreement with experiment. At the time, the quadrupole moments so deduced seemed quite reasonable,<sup>5</sup> but they can no longer be substantiated. The rare-gas atoms, for example, are now known to be spherically symmetrical, thus possessing no permanent moments of any order.

Another fundamental objection to the exclusive use of Equation (70.1), or its quadrupole extension, for the attractive forces lies in the fact that the orientation effect, as indicated in Equation (70.3), vanishes for high temperatures, although experimental results indicate that the van der Waals forces do not behave in this way. It is therefore imperative to consider the effects of one molecule on the electron cloud of the other, as mentioned earlier. Of course, this does not mean that Equation (70.1) should be altogether abandoned, for it yields an important contribution to the long-range forces between polar molecules, as will be seen in Section 83.

**(71) Induction Effect:** To obtain the van der Waals energy of two molecules from Equation (69.2) by averaging over all phases of the electronic motions, it is necessary to use quantum-mechanical methods. However, if at least one of the molecules possesses a permanent electrostatic moment, a part of this energy can be treated classically, as first shown by Debye<sup>1</sup> and extended by Falkenhagen;<sup>2</sup> this is the part due to the interaction of the permanent moment of one molecule with the electron-cloud of the other.

When a molecule is placed in an electric field of strength  $\mathbf{F}$ , a dipole moment  $\mathbf{m} = \alpha\mathbf{F}$  is induced in it by the field, where  $\alpha$  is the polarizability,<sup>3</sup> and the accompanying change in potential energy is given by

$$- \int \mathbf{m} \cdot d\mathbf{F} = - \alpha F^2/2 \quad (71.1)$$

If we consider the interaction of two molecules, the field of each molecule will polarize the electron-cloud of the other, and the resulting contribution to the potential energy will be

$$u = - (\alpha_1 F_2^2 + \alpha_2 F_1^2)/2 \quad (71.2)$$

Now the field  $\mathbf{F}$  of a molecule at a point  $\mathbf{R}$  from its center can be evaluated from

<sup>5</sup> A remarkable coincidence, mentioned by Margenau (*loc. cit.*), deserves attention. For the hydrogen molecule, Keesom found a quadrupole constant  $\tau$  (see Section 71) of  $2.03 \times 10^{-26}$  e.s.u. to give the best fit of the equation of state, while a value of  $2.05 \times 10^{-26}$  had been calculated for this molecule from the old quantum theory, for a molecular model now known to be incorrect. Modern theory leads to a value of only about  $0.4 \times 10^{-26}$ .

<sup>1</sup> P. Debye, *Physik. Z.*, 21, 178 (1920).

<sup>2</sup> H. Falkenhagen, *Physik. Z.*, 23, 87 (1922).

<sup>3</sup> For anisotropic molecules,  $\alpha$  is a tensor; i.e., the induced moment depends on the orientation of the molecule with respect to the field. In general,  $\alpha$  depends on frequency for alternating fields, but this section is concerned only with the static value of  $\alpha$ .

Equation (69.1); for example, if the molecule has a dipole moment  $\mu$  we obtain

$$F^2 = |-\text{grad } \phi|^2 = \mu^2(1 + 3 \cos^2 \theta)/R^6 \quad (71.3)$$

where  $\theta$  is the angle between  $\mathbf{u}$  and  $\mathbf{R}$ . Since the resulting contribution to the van der Waals energy turns out to be only a small fraction of the total, we shall be content to average  $F^2$  at once over all orientations, using  $\langle \cos^2 \theta \rangle_{\text{av}} = \frac{1}{3}$ . Equations (71.2) and (71.3) then yield

$$u = -(\alpha_1 \mu^2 + \alpha_2 \mu^2)/R^6 \quad (71.4)$$

for the "induction effect" due to permanent dipoles.<sup>4</sup>

The induction energy due to permanent quadrupoles can also be obtained from Equation (69.1), and after averaging over all orientations is found to be

$$u = -3(\alpha_1 \tau^2 + \alpha_2 \tau^2)/2R^8, \quad (71.5)$$

where  $\tau$  is defined in terms of the principal quadrupole moments<sup>5</sup>  $\Theta_i$  by the relation

$$\tau^2 = \frac{1}{2} \sum_{i>j}^3 (\Theta_i - \Theta_j)^2 \quad (71.6)$$

While the induction effect, unlike the orientation effect of Section 70, does not vanish at high temperatures, it also fails to account for the existence of van der Waals forces between the rare-gas atoms, or for the magnitude of the attractive forces in general. As will be shown in the following section, the interaction due to *instantaneous* (rather than permanent) dipoles contributes the major effect, the induction energy always playing a secondary role.

(72) **Dispersion Effect:** As hinted in earlier paragraphs, the mutual perturbations of the electron clouds of two atoms or molecules give rise to a major portion of the van der Waals forces. Between molecules in their ground electronic states, these forces are always attractive. Their principal part is due to interactions between the instantaneous dipole moments, and gives (like the induction effect, to which it is not unrelated) a potential energy varying inversely as the sixth power of the intermolecular separation. First noticed by Wang,<sup>1</sup> these forces were fully and generally interpreted by London,<sup>2</sup> who showed their intimate connection with the optical properties of the molecules

<sup>4</sup> Our statement that the induction effect can be treated "classically" is true up to this point, and this is usually sufficient, since  $\alpha$  and  $\mu$  can be experimentally determined. More fundamentally, of course, theoretical prediction of  $\alpha$  and  $\mu$ , as of any atomic or molecular property, would require quantum-mechanical methods.

<sup>5</sup> Like a moment of inertia, the quadrupole moment in general has six components, such as  $\sum e_i x_i^2$ ,  $\sum e_i x_i y_i$ , etc., but it is always possible to find three mutually perpendicular axes in the molecule which cause the cross-products to vanish, leaving the three principal moments  $\Theta_1 = \sum e_i x_i^2$ ,  $\Theta_2 = \sum e_i y_i^2$ , and  $\Theta_3 = \sum e_i z_i^2$ . It can be seen from Equation (71.6) that  $\tau$  vanishes for molecules with spherically symmetrical distributions of charge.

<sup>1</sup> S. C. Wang, *Physik. Z.*, 28, 663 (1927).

<sup>2</sup> (a) F. London, *Z. physik. Chem.*, B11, 222 (1930); (b) R. Eisenschitz and F. London, *Z. Physik*, 60, 491 (1930); (c) F. London, *ibid.*, 63, 245 (1930).

and hence gave them the name *dispersion effect*. In recent years, they have often appropriately been called "London forces."

Full mathematical treatment of the dispersion effect<sup>3</sup> requires quantum mechanics, but useful results may be gained from a simplified treatment requiring a minimum of quantum-mechanical knowledge. With London, we consider an atomic model consisting of an electron bound by a linear restoring force to a fixed and massive equally charged nucleus; this is the harmonic-oscillator model used by Lorentz and others in developing the classical theory of dispersion. Placing two such (similar) atoms at an internuclear distance  $R$  from each other, so that their charges interact, we have a total potential energy

$$V = (kr^2/2) + (kp^2/2) + (e^2/R^3)(x\xi + y\eta - 2z\zeta) + \dots \quad (72.1)$$

in which  $k$  is the restoring-force constant and the two electrons are located at distances  $r(x, y, z)$  and  $\rho(\xi, \eta, \zeta)$  from their respective nuclei. The last term is clearly the dipole-dipole interaction of Equation (69.2). Classically, if this interaction were absent, the two electrons would act independently, each executing harmonic motion with a frequency  $\nu_0 = (k/m)^{1/2}/2\pi$ , where  $m$  is the electron mass. According to quantum mechanics, the lowest possible energy of such an independent (three-dimensional) oscillator is  $3h\nu_0/2$ , or  $h\nu_0/2$  for each degree of freedom,  $h$  being the Planck constant.

When the interaction is introduced, the oscillators are thereby coupled, and the problem is conveniently solved by changing to a set of normal coordinates<sup>4</sup> which are linear combinations of the original coordinates. In the present problem, the normal coordinates are given by

$$X_1 = 2^{-1/2}(x + \xi), \quad X_2 = 2^{-1/2}(x - \xi)$$

with similar definitions for the  $y$ - and  $z$ -components. In terms of these coordinates, the potential energy becomes

$$V = \frac{1}{2} \left( k + \frac{e^2}{R^3} \right) (X_1^2 + Y_1^2) + \frac{1}{2} \left( k - \frac{e^2}{R^3} \right) (X_2^2 + Y_2^2) \\ + \frac{1}{2} \left( k - \frac{2e^2}{R^3} \right) Z_1^2 + \frac{1}{2} \left( k + \frac{2e^2}{R^3} \right) Z_2^2 \quad (72.2)$$

and the kinetic energy also contains only square terms. The six frequencies corresponding to each of the normal coordinates may then be written down at once:

$$\nu(X_1) = \nu(Y_1) = \nu_0 \left( 1 + \frac{e^2}{kR^3} \right)^{1/2} \\ \nu(X_2) = \nu(Y_2) = \nu_0 \left( 1 - \frac{e^2}{kR^3} \right)^{1/2} \\ \nu(Z_1) = \nu_0 \left( 1 - \frac{2e^2}{kR^3} \right)^{1/2}, \quad \nu(Z_2) = \nu_0 \left( 1 + \frac{2e^2}{kR^3} \right)^{1/2} \quad (72.3)$$

<sup>3</sup> Consult the papers of London, *loc. cit.*, or the review article by Margenau, *loc. cit.*

<sup>4</sup> See, for example, J. C. Slater and N. H. Frank, *Mechanics* (McGraw-Hill, 1947), Chap. VII.

The ground-state energy of the coupled system is then simply  $h/2$  times the sum of these six frequencies. Since the interaction term is small compared to the binding force within each atom, we may expand the square roots, and after subtracting the zero-point energy  $3h\nu_0$  of the two uncoupled oscillators (i.e., corresponding to infinite separation) we obtain the interaction energy

$$u = -3h\nu_0 e^4 / 4k^2 R^6 + \quad (72.4)$$

Now according to this same atomic model the (static) polarizability of an atom is very simply related to the force-constant  $k$  by the expression  $\alpha = e^2/k$ . With this substitution, the interaction energy becomes

$$u = -3h\nu_0 \alpha^2 / 4R^6 \quad (72.5)$$

The molecular constants in this formula can be derived from experiment,  $\alpha$  from the refractive index extrapolated to long wave-lengths and  $\nu_0$  from the variation of refractive index with frequency (i.e., dispersion).<sup>5</sup>

The validity of Equation (72.5) may be questioned, primarily of course because of the highly fictitious atom model employed. However, the parameter  $\alpha$  was introduced in place of the force-constant  $k$  by a relation which made use of the same model, and the final expression contains only experimentally observable quantities; thus, the shortcomings of the model may optimistically be thought to have been largely canceled. It will later be seen that Equation (72.5) is in fact correct whenever the dispersion can be adequately described in terms of a single frequency  $\nu_0$ , as is sometimes the case.

TABLE VI  
POLARIZABILITIES AND DIAMETERS OF MOLECULES

Gas	$\alpha(\text{\AA}^3)$	$\sigma(\text{\AA})^1$	$\alpha/\sigma^3$
He.....	.204	2.56	.0122
Ne.....	.392	2.74	.0190
A.....	1.63	3.41	.0411
Kr.....	2.465	3.59	.053
Xe.....	4.01	4.06	.060
H <sub>2</sub> .....	0.81	2.92	.0325
N <sub>2</sub> .....	1.74	3.65	.0358
CH <sub>4</sub> .....	2.58	3.79	.0473

<sup>1</sup> See Table X, Section 81.

A second question concerns the expansions made in going from (72.3) to (72.4), for these will be rapidly convergent only if  $e^2/kR^3 (= \alpha/R^3)$  is much less than unity. In Table VI are given the ratios  $\alpha/\sigma^3$  for several gases, where  $\sigma$  is the distance at which the attractive energy is just equal to the short-range

<sup>5</sup> See, for example, J. C. Slater and N. H. Frank, *Electromagnetism* (McGraw-Hill, 1947), Chap. IX, or S. Dushman, this Treatise, Vol. I, p. 357.



repulsive energy (Section 73); that is,  $\sigma$  is roughly the "molecular diameter." It is seen that  $\alpha/\sigma^3$  is small in all cases, indicating that Equation (72.5), if otherwise correct, may be used for all separations exceeding  $\sigma$ .

Another derivation of the dispersion energy can be based on the same atom model used above, but is more closely related to the considerations of Section 71. This will be presented here for the interaction between two unlike atoms, for which it is more convenient than the normal-coordinate method; it also provides a more direct route to the general formula to be given later. In this method, the interaction is regarded as an induction effect, and is therefore to be evaluated from Equation (71.4). However, the dipole moments involved are not static, but are due to oscillating dipoles, so that the static polarizabilities must be replaced by dynamic values appropriate to the frequencies of the oscillators. These are given <sup>6</sup> by the relation

$$\begin{aligned}\alpha_1(\nu) &= (e^2/4\pi^2m)/(\nu_1^2 - \nu^2) \\ &= \alpha_1^0\nu_1^2/(\nu_1^2 - \nu^2)\end{aligned}\quad (72.6)$$

where  $\alpha_1(\nu)$  is the polarizability of an electron oscillator of natural frequency  $\nu_1$  in an alternating field of frequency  $\nu$ , and  $\alpha_1^0$  represents its static value. Considering the interaction of two unlike oscillators, we then have

$$u = -R^{-6}[\alpha_1(\nu_2)\mu_2^2 + \alpha_2(\nu_1)\mu_1^2] \quad (72.7)$$

The squares of dipole moments must be taken as average values over all phases of the motion; e.g.,  $\mu_1^2 = e^2\langle r_1^2 \rangle_{Av}$ . These are easily found by use of the well-known result that the average potential energy of an harmonic oscillator is half of its total energy.<sup>7</sup> Writing this condition as

$$\frac{1}{2}k_1\langle r_1^2 \rangle_{Av} = \frac{1}{2}(3/2\hbar\nu_1)$$

and recalling the relation  $\alpha_1^0 = e^2/k_1$  for the static polarizability, we obtain

$$\begin{aligned}\mu_1^2 &= 3\hbar\nu_1\alpha_1^0/2 \\ &= 3\hbar e^2/8\pi^2m\nu_1\end{aligned}\quad (72.8)$$

with similar relations for  $\mu_2^2$ . Use of Equations (72.6) and (72.8) in Equation (72.7) then gives

$$u = -\frac{3\hbar}{2R^6} \frac{\alpha_1^0\alpha_2^0\nu_1\nu_2}{\nu_1 + \nu_2} \quad (72.9)$$

which reduces to Equation (72.5) for two identical atoms. This result will later be useful in considering attractive forces between unlike molecules in gas mixtures. By making use of Equation (72.6) or (72.8), it may also be put in the alternative forms

$$-uR^6 = \frac{3\hbar e^4}{32\pi^4m^2\nu_1\nu_2(\nu_1 + \nu_2)} = \frac{2\mu_1^2\mu_2^2}{3\hbar(\nu_1 + \nu_2)} \quad (72.10)$$

<sup>6</sup> Dushman, *loc. cit.*, p. 357.

<sup>7</sup> This is true whether classical or quantum mechanics are used.

In general, the behavior of a single oscillator does not adequately reproduce the dispersion curve accurately, and a better model of the atom would consist of  $f_a, f_b, \dots, f_i, \dots$  electronic oscillators with corresponding natural frequencies  $\nu_a, \nu_b, \dots, \nu_i, \dots$ . For this model, the extensions of Equations (72.6) and (72.8) are

$$\alpha(\nu) = (e^2/4\pi^2 m) \sum f_i/(\nu_i^2 - \nu^2) \quad (72.6')$$

$$\mu^2 = \sum \mu_i^2 \quad (3\hbar e^2/8\alpha^2 m) \sum_i f_i/\nu_i \quad (72.8')$$

Thus the field due to an atom is now made up of components oscillating at various frequencies. When these formulae are used in Equation (72.7), with subscripts  $l$  and  $\lambda$  denoting the various kinds of oscillators in the first and second atoms, respectively, the interatomic energy is given by

$$-uR^6 = \frac{3\hbar e^4}{32\pi^4 m^2} \sum_i \sum_\lambda \frac{f_i f_\lambda}{\nu_i \nu_\lambda (\nu_i + \nu_\lambda)} - \frac{2}{3\hbar} \sum_i \sum_\lambda \frac{\mu_i^2 \mu_\lambda^2}{\nu_i + \nu_\lambda} \quad (72.11)$$

from which the earlier special formula of Equation (72.10) is easily recovered.

The above equation, although based on the fictitious model of an atom as a collection of harmonically oscillating electrons, is actually the correct general result;<sup>8</sup> it is only necessary to alter the physical interpretations of the quantities  $\nu_i$ ,  $f_i$ , and  $\mu_i$ . In quantum mechanics an atom is characterized by a set of stationary quantum states  $l$ , with energy levels  $\epsilon_l$  and wave functions  $\psi_l$ . When the quantum theory of dispersion is carried through, by the methods of perturbation theory, the polarizability of an atom in its ground state (subscript zero in the following equations) is found<sup>9</sup> to be given by Equation (72.6') and its mean square moment by (72.8'), together with the following relations:

$$\begin{aligned} \nu_i &= (\epsilon_i - \epsilon_0)/\hbar \\ \mu_i &= e \int \psi_0(\sum_i \mathbf{r}_i) \psi_i d\tau \\ f_i &= 8\pi^2 m \nu_i \mu_i^2 / 3\hbar e^2 \end{aligned} \quad (72.12)$$

In the second of these equations,  $\mathbf{r}_i$  denotes the coordinate of the  $i$ th electron, and the integration extends over all electron configuration space. It is seen that the natural frequencies  $\nu_i$  of the fictitious harmonic oscillators are actually to be identified with the various absorption frequencies of an atom in its ground state. The oscillator strengths  $f_i$  may be derived from the intensities of the corresponding spectral lines; they represent the equivalent numbers of classical oscillators of frequency  $\nu_i$ , but are usually not integral.

Evaluation of the interaction energy between two atoms by quantum-mechanical perturbation theory, with Equation (69.2) as the perturbation

<sup>8</sup> For atoms with ground  $S$ -states. Forces between atoms in  $P$ - or  $D$ -states, or between excited atoms, need not be considered for our purpose.

<sup>9</sup> Dushman, *loc. cit.*, pp. 344-359.

energy, leads to no first-order contribution, but the second-order term gives Equation (72.11) exactly.<sup>10</sup>

If the absolute intensities of all the spectral lines (including the continuum) of two atoms are well known, the dispersion energy could be precisely calculated from Equation (72.11), but save for the practically unimportant case of atomic hydrogen (where  $f_i$  can be theoretically evaluated with precision) this knowledge is not available. More often, recourse must be had to an empirical dispersion formula of the type of (72.6') or even of (72.6); when even the latter are lacking, an approximate value may be obtained with Equation (72.5) by taking the polarizability for any available frequency and identifying  $h\nu_0$  with the ionization potential. Empirically it appears that these estimates are usually too low.

Since Equation (72.11) can so rarely be used to full advantage, many calculations of the dispersion energy have been based on the variation method.<sup>11</sup> We have space here only for an approximate formula due to Slater and Kirkwood:<sup>12</sup>

$$-uR^6 = \frac{3he}{4\pi m^{1/2}} \frac{\alpha_1 \alpha_2}{(\alpha_1/N_1)^{1/2} + (\alpha_2/N_2)^{1/2}} \quad (72.13)$$

which reduces for two similar molecules to

$$-uR^6 = 3heN^{1/2}\alpha^{3/2}/8\pi m^{1/2} \quad (72.13')$$

In these formulae, the number  $N$  represents a number of electrons in the atom; Slater and Kirkwood<sup>12(a)</sup> considered it to be the number of electrons in the outermost shell, but with an alternative derivation Kirkwood<sup>12(b)</sup> used the total number in the atom. The latter alternative assigns equal weight to each electron, whether in an inner or outer shell of the atom, and it is certain, especially from the detailed study of argon by Knipp,<sup>13</sup> that this gives too large a result; we shall therefore employ it in Section 81 to provide an upper limit to the theoretical value. Hellmann<sup>14</sup> and Buckingham<sup>15</sup> have improved on Equation (72.13) by providing similar formulae in which the contributions of the inner electron-shells in an atom are neither ignored nor exaggerated, but again the required information for their use is usually lacking.

An interesting comparison of the Slater-Kirkwood formula with that of London is afforded by specializing Equation (72.11) to the case of two like atoms, each with a single frequency and oscillator strength and using Equation (72.6') to eliminate the frequency. This procedure gives

$$-uR^6 = 3hef^{1/2}\alpha^{3/2}/8\pi m^{1/2} \quad (72.14)$$

<sup>10</sup> F. London, *Z. physik. Chem.*, **B11**, 222 (1930).

<sup>11</sup> See, for example, Pauling and Wilson, *loc. cit.*, pp. 180-190, 383-388; or the review article by Margenau, *loc. cit.*, pp. 24-28.

<sup>12</sup> (a) J. C. Slater and J. G. Kirkwood, *Phys. Rev.*, **37**, 682 (1931); (b) J. G. Kirkwood, *Physik. Z.*, **33**, 57 (1932).

<sup>13</sup> J. K. Knipp, *Phys. Rev.*, **55**, 1244 (1939).

<sup>14</sup> H. Hellmann, *Acta Physicochimica URSS*, **2**, 273 (1935).

<sup>15</sup> R. A. Buckingham, *Proc. Roy. Soc. (London)*, **A160**, 94 (1937).

which is identical with (72.13') if  $f$  is substituted for  $N$ . Empirical one-term dispersion formulae usually make  $f$  less than even the number of electrons in the outer shell, so that Equation (72.14) (or its equivalent [72.5]) is probably a lower limit; it has been so regarded in Section 81.

When applied exhaustively, the variational method does not yield any simple expression such as Equation (72.13), but gives a result depending more intimately on the atomic wave functions employed. Many such calculations have been made for helium, and in the most detailed of these Baber and Hassé<sup>16</sup> found a dispersion effect almost identical with that obtained by Margenau<sup>17</sup> from Equation (72.11) with a two-term dispersion formula.

Returning to the general formula of Equation (72.11), we observe that the strongest dispersion forces should arise between molecules which absorb strongly at long wave-lengths. An interesting application of this conclusion has been made by Rabinowitch and Epstein,<sup>18</sup> who attribute the association of dyestuff molecules in dilute solution to a large dispersion effect.

TABLE VII  
MAGNITUDES OF THE SEVERAL CONSTITUENTS OF THE VAN DER WAALS FORCES<sup>a</sup>

Gas	$\mu \cdot 10^{18}$ (e.s.u.)	$\alpha \cdot 10^{24}$ (cm. <sup>3</sup> )	$h\nu$ (e.v.)	Orientation Effect	Induction Effect	Dispersion Effect
				$2\mu^4$ 3(293K) (erg cm. <sup>6</sup> )	$2\mu^2\alpha \cdot 10^{60}$ (erg cm. <sup>6</sup> )	$\frac{3}{4}\alpha^2 h\nu_0 \cdot 10^{60}$ (erg cm. <sup>6</sup> )
CO...	0.12	1.99	14.3	0.0034	0.057	67.5
HI...	0.38	5.4	12	0.35	1.68	382
HBr...	0.78	3.58	13.3	6.2	4.05	176
HCl...	1.03	2.63	13.7	18.6	5.4	105
NH <sub>3</sub> ...	1.5	2.21	16	84	10	93
H <sub>2</sub> O...	1.84	1.48	18	190	10	47

<sup>a</sup> F. London, *Trans. Faraday Soc.*, **33**, 8 (1937).

It is now pertinent to compare the magnitudes of the various components of the van der Waals forces. In Table VII, taken from London, this is done for some simple polar molecules. The last three columns give the coefficients of  $R^{-6}$  in: (a) the averaged orientation effect at 20°C, from Equation (70.3); (b) the induction effect, from Equation (71.4); and (c) the dispersion effect, from the one-term formula of Equation (72.5). The magnitudes used in the calculation are given in the previous columns, and are representative of those for simple molecules. It can be seen that the dispersion energy is much the largest for all but the most highly polar gases, and that the induction effect

<sup>16</sup> T. D. H. Baber and H. R. Hassé, *Proc. Camb. Phil. Soc.*, **33**, 253 (1937).

<sup>17</sup> H. Margenau, *Phys. Rev.*, **56**, 1000 (1939)

<sup>18</sup> E. Rabinowitch and L. F. Epstein, *J. Am. Chem. Soc.*, **63**, 69 (1941).

always plays a minor role. In non-polar molecules, of course, the dispersion effect alone remains.

If Equation (69.2) is extended to include interactions involving quadrupoles and higher-order multipoles, new contributions to the dispersion effect arise. The general result is a series

$$= -C_1 R^{-6} - C_2 R^{-8} - C_3 R^{-10} - \quad (72.15)$$

in which the first term is the dipole-dipole contribution thus far discussed, the second term comes from dipole-quadrupole interactions, the next from both quadrupole-quadrupole and dipole-octupole interactions, and so on. The second and third terms have been studied specially for atomic hydrogen<sup>19</sup> and for helium,<sup>20</sup> but the only general treatment is that of Margenau<sup>21</sup> for the simple harmonic oscillator model. For two similar molecules, the results are

$$\begin{aligned} C_2 &= 15\alpha^3(h\nu)^2/4fe^2 = 15h^2\alpha^2/16\pi^2m \\ C_3 &= 735\alpha^4(h\nu)^3/32f^2e^4 = 735h^3\alpha^5/256\pi^3ef^{1/2}m^{3/2} \end{aligned} \quad (72.16)$$

These equations yield values of  $C_2$  and  $C_3$  in fair agreement with the more trustworthy special results for H and He, and thus may be considered to yield useful results. Investigation of the magnitudes involved shows that the dipole-quadrupole term contributes appreciably to the total attractive potential at distances near the equilibrium separation of the two molecules, but that the higher terms can be neglected in all cases of interest.

When the molecules are not spherically symmetrical, the dispersion forces will also depend on the orientations of the molecules as well as on their separation. If the molecules are rigid, a first approximation is furnished by the harmonic oscillator model, but with the use of *anisotropic* oscillators.<sup>22,23</sup> For chain molecules, it is tempting to regard each chain atom as a center of a spherically symmetrical force field, and to treat the total interaction between the molecules as the sum between such pairs of force-centers. London has shown that this model cannot be exact, particularly in the case of a conjugated unsaturated chain (polyene), but for saturated molecules it is probably a reasonably good approximation.<sup>24</sup> More detailed calculations of the dispersion forces between asymmetrical molecules have been made only for hydrogen.<sup>25</sup> In practice, as will later be seen, the asymmetry may often be ignored.

<sup>19</sup> H. Margenau, *Phys. Rev.*, **38**, 747 (1931); L. Pauling and J. Y. Beach, *Phys. Rev.*, **47**, 686 (1935).

<sup>20</sup> H. Margenau, *Phys. Rev.*, **38**, 747 (1931); R. A. Buckingham, *Proc. Roy. Soc. (London)*, **A160**, 94 (1937); C. H. Page, *Phys. Rev.*, **53**, 426 (1938).

<sup>21</sup> H. Margenau, *J. Chem. Phys.*, **6**, 896 (1938), as amended by R. Heller, *J. Chem. Phys.*, **9**, 154 (1941).

<sup>22</sup> J. H. de Boer and G. Heller, *Physica*, **4**, 1045 (1937).

<sup>23</sup> F. London, *J. Phys. Chem.*, **46**, 305 (1942).

<sup>24</sup> The application of such a model is considered in Section 82.

<sup>25</sup> H. S. W. Massey and R. A. Buckingham, *Proc. Roy. Irish Acad.*, **A45**, 31 (1938); J. de Boer, *Physica*, **9**, 363 (1942); H. Margenau, *Phys. Rev.*, **63**, 131 (1943).

(73) **Exchange Forces; Repulsions at Short Range:** Physically, the low compressibility of very dense gases and of liquids and solids shows unequivocally that when molecules are brought sufficiently close together their attractive forces are overshadowed by strong repulsions. In classical kinetic theory, these repulsions were introduced by regarding the molecules as hard impenetrable spheres of definite size. The success of this model, which is still adequate for the treatment of many phenomena, shows that the repulsive forces are quite suddenly encountered when the intermolecular separation is decreased. With the discovery of the nuclear atom, the hard-sphere molecule became a fiction<sup>1</sup> requiring explanation in terms of the electrostatic forces between electrons and nuclei. This explanation was given by Heitler and London<sup>2</sup> in 1927, simultaneously with their elucidation of covalent chemical binding, to which it is closely related. The Pauli exclusion principle plays a dominant role in both phenomena.

The Heitler-London discussion of the hydrogen molecule<sup>3</sup> is illustrative of the situation in general. When the two hydrogen atoms are made to approach closely, their charge clouds begin to overlap appreciably. If the spins of the two electrons are antiparallel, the electronic wave function of the system, to satisfy the exclusion principle, must be symmetrical in the coordinates of these electrons, and this leads mathematically to prediction of a large electron density between the nuclei, accompanied by a strong attraction down to a minimum energy at a separation of 0.74 Å. However, if the spins are parallel, the antisymmetrical wave function is required, and in this case the electron density between the nuclei is greatly reduced, with intermolecular repulsion at all distances.<sup>4</sup> Effectively, the exclusion principle sets an upper limit to the concentration of unpaired electrons, so that when two atoms are forced close together such electrons must seek other regions of space. The work of thus distorting the atoms appears as the repulsive energy between them. Now, almost all chemically stable atoms and molecules have only completely filled electron-shells, with all electrons already "paired" with respect to electron spin; the only permissible state of a system of two such molecules is therefore that analogous to the repulsive state of hydrogen.<sup>5</sup> Since this repulsion becomes important when the two charge distributions overlap appreciably, it has sometimes been called the "overlap energy."

<sup>1</sup> In view of the fact that the compressibility of any substance never vanishes, it was early recognized that the molecules could not be *perfectly* impenetrable or incompressible.

<sup>2</sup> W. Heitler and F. London, *Z. Physik*, **44**, 455 (1927).

<sup>3</sup> Dushman, this Treatise, 3d. ed., Vol. I, pp. 419-425.

<sup>4</sup> The Heitler-London calculation is that of the first-order perturbation energy, and the attractive dispersion forces, which must dominate at large separations, appear only in the second-order term.

<sup>5</sup> Even for the attractive covalent state of two atoms with unfilled shells, such as hydrogen or chlorine atoms, repulsions between closed inner shells or the bare nuclei eventually predominate at small enough separations, thus fixing the lengths of valence bonds.

Mathematically, the repulsive energy can be calculated from the perturbation theory of quantum mechanics:

$$\int v\psi_0^2 d\tau + \quad (73.1)$$

In this equation,  $\psi_0$  is the ("unperturbed") electronic wave-function for the system of two independent, non-interacting molecules, but satisfying the exclusion principle for the two-molecule system, and  $v = \sum e_i e_j / r_{ij}$  is the coulombic potential energy of the forces between the electrons and nuclei of one molecule and those of the other. The expansion of  $v$  in inverse powers of  $R$ , as in Equation (69.2), is no longer convergent when the electron clouds overlap appreciably, and the unexpanded form must be used directly. For the case of covalent binding, the first-order perturbation energy of Equation (73.1), while disclosing the essential features, falls considerably short of quantitative success, so that higher-order perturbation calculations or variational methods must be used. However, for the repulsions between closed shells the first-order calculation is fortunately almost sufficient. When this calculation is carried through, the principal contributions to  $u$  are found to arise from terms in  $\psi_0^2$  corresponding to the "exchange" of a single pair of electrons between the two atoms (in this case, electrons with parallel spins); thus the repulsive forces may be regarded largely as "exchange forces," just as those leading to covalent bonds. This is quite clear from the Heitler-London treatment of the hydrogen molecule.

The mathematical difficulties (and tedium) involved in these calculations are great, and they have been carried out in detail only for hydrogen atoms, helium,<sup>6</sup> neon,<sup>7</sup> and hydrogen molecules.<sup>8</sup> In almost all of these treatments, highly approximate wave-functions  $\psi_0$  have been used, in order to get tractable results. The most accurate calculation is probably that of Slater for helium. Although the analytical results were complicated (compare even the Heitler-London result for the atomic hydrogen repulsions!), he found that a simple exponential relationship,

$$u = A \exp(-R/\rho) \quad (73.2)$$

with  $A = 7.70 \times 10^{-10}$  erg,  $\rho = 0.218 \text{ \AA}$ , reproduced the numerical values excellently over the range of physical importance ( $R > 1 \text{ \AA}$ ). Later Bleick and Mayer used a similar expression, with  $A = 1.88 \times 10^{-8}$  erg and  $\rho = 0.209 \text{ \AA}$ , to represent their calculated values for neon, and Born and Mayer<sup>9</sup> were able to correlate the properties of *all* the alkali halide crystals by using the value  $\rho = 0.345 \text{ \AA}$  for repulsions involving any pair of ions. Thus the constant  $\rho$ , which is the distance over which the repulsions fall by a factor  $e$ , seems to have

<sup>6</sup> (a) J. C. Slater, *Phys. Rev.*, **32**, 349 (1928); (b) G. Gentile, *Z. Physik*, **63**, 795 (1930); (c) N. Rosen, *Phys. Rev.*, **38**, 255 (1931); (d) M. F. Mamotenko, *Acta Physicochimica URSS*, **11**, 225 (1939).

<sup>7</sup> W. E. Bleick and J. E. Mayer, *J. Chem. Phys.*, **2**, 252 (1934).

<sup>8</sup> (a) J. de Boer, *Physica*, **9**, 363 (1942); (b) H. Margenau, *Phys. Rev.*, **63**, 131 (1943).

<sup>9</sup> M. Born and J. E. Mayer, *Z. Physik*, **75**, 1 (1932).

roughly the same value for most atoms and ions. The factor  $A$ , however, is not easily predictable and must usually be determined from experimental results.

Other empirical forms than Equation (73.2) are often used to represent the repulsive energy. Wasastjerna<sup>10</sup> has discussed crystals with the aid of a repulsive energy term

$$u = aR^7 \exp(-bR) \quad (73.3)$$

and developed rules regarding the magnitudes of  $a$  and  $b$ . An inverse-power law,

$$u = \lambda R^{-n} \quad (73.4)$$

has been in frequent use since the time of Maxwell, and for reasons of mathematical convenience is still generally preferred to the exponential form of Equation (73.2), although it is doubtless less correct. This will be more fully considered in Section 81. Of course, the hard-sphere model itself must be regarded as an extreme but still useful approximation to the repulsive energy. The successful exploitation of the concept of definite ionic radii and atomic "van der Waals radii" is, for example, well illustrated in the work of Pauling.<sup>11</sup>

Finally, it may be mentioned that repulsive forces can be calculated, though not with high precision, by application of the Thomas-Fermi statistical atom model. The results of such calculations are fully described in a recent book.<sup>12</sup>

(74) **The Complete Potential Energy Between Two Molecules:** Expressions for the total interaction between two molecules may now be constructed from the equations for the various "effects" described in previous paragraphs, and their applications to gases will follow. The simplest case is that of two spherically symmetrical non-polar atoms or molecules, for which the potential energy depends only on the separation <sup>1</sup>  $r$  between their centers of mass. The most elementary function possessing utility combines hard-sphere repulsion (molecular "diameter"  $\sigma$ ) with the dipole-dipole dispersion effect:

$$\begin{aligned} u &= -Cr^{-6} & (r \geq \sigma) \\ &\rightarrow \infty & (r < \sigma) \end{aligned} \quad (74.1)$$

Replacement of the hard sphere by an inverse-power repulsion gives the expression

$$u = \lambda r^{-n} - Cr^{-6} \quad (n > 6) \quad (74.2)$$

first applied to physical problems by Lennard-Jones (see Section 81). The power  $n$  which best combines agreement with experiment and mathematical

<sup>10</sup> J. A. Wasastjerna, *Soc. Sci. Fennicae, Comm. Phys.-Math.*, 6, nos. 18-22 (1932).

<sup>11</sup> L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, 1940), particularly Chaps. V and X.

<sup>12</sup> P. Gombás, *Die Statistische Theorie des Atoms und ihre Anwendungen* (Vienna: Springer, 1949).

<sup>1</sup> In previous paragraphs the intermolecular distance was conveniently written as  $R$ ; from now on,  $r$  will be used.



convenience is 12; a plot of the resulting potential function is shown in Fig. 6. When the repulsive index  $n$  is specified, the Lennard-Jones potential is characterized by two constants,  $\lambda$  and  $C$ , but it is more convenient to replace these by the energy value  $\epsilon$  measuring the depth of the potential well and by either  $\sigma$  or  $r_0$ , the distances at the zero or minimum. In terms of these constants, Equation (74.2) becomes (for  $n = 12$ )

$$u = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]; \quad \epsilon = C^2/4\lambda; \quad \sigma^6 = \lambda/C \quad (74.3)$$

or

$$u = \epsilon[(r_0/r)^{12} - 2(r_0/r)^6]; \quad r_0^6 = 2\sigma^6 \quad (74.4)$$

If the inverse-power repulsion is replaced by Slater's exponential form, the potential energy becomes

$$u = Ae^{-r/\rho} - Cr^{-6} \quad (74.5)$$

which may be written in terms of  $\epsilon$  and  $r_0$  as

$$u = \left(\frac{6}{\alpha - 6}\right) \epsilon \left[ e^{-\alpha\left(\frac{r}{r_0} - 1\right)} - \frac{\alpha}{6} \left(\frac{r_0}{r}\right)^6 \right]; \quad \alpha = r_0/\rho \quad (74.6)$$

As will be seen later, Equation (74.5) is probably adequate for dealing with almost all phenomena involving interactions between spherical molecules, but

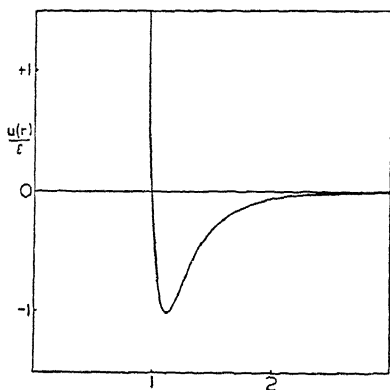


FIG. 6. Potential energy between a pair of spherical non-polar molecules according to Lennard-Jones, Eq. (74.3), as a function of the intermolecular separation  $r$ .

further refinements may be added. One of these is the inclusion of higher-pole contributions to the dispersion effect, that in  $r^{-8}$  (from dipole-quadrupole interactions) being appreciable; another requires more discussion. It will be seen that in Equations (74.2) and (74.5) we have been grafting together an expression for the repulsive energy, as evaluated for small distances by first-order perturbation theory, and one for the dispersion energy, as obtained for large distances by second-order perturbation theory. Is this procedure self-consistent, and does it yield correct results at distances where both terms are of comparable magnitude, i.e., in the very important region around the zero and minimum of the curve? The fact

is that a portion of the second-order perturbation energy, namely that arising in this order from the "exchange" terms of the wave-function, has been ignored. Investigating these terms, Margenau<sup>2</sup> found them to be by no means negligible for atomic hydrogen, but quite small (though not completely

<sup>2</sup> H. Margenau, *Phys. Rev.*, **56**, 1000 (1939).

negligible) and negative for helium, and he concluded that they would also be small for all other stable molecules. For helium, Margenau constructed the potential energy

$$u \times 10^{12} = 770e^{-4.60r} - 560e^{-5.33r} - 1.39r^{-6} - 3.0r^{-8} \quad (u \text{ in erg, } r \text{ in } \text{\AA}) \quad (74.7)$$

in which the second term is the second-order exchange energy; the nature of the other terms is readily recognized. The second-order exchange contributes about five per cent of the absolute value of  $u$  at the minimum. For practical purposes, it may be combined with the dipole-quadrupole term by increasing the numerical coefficient of the latter from 3.0 to 3.7.

For non-spherical non-polar molecules, the terms thus far introduced into  $u$  all become dependent on orientation, and the orientation and induction effects involving quadrupoles enter as well. However, the average orientation effect vanishes, the induction effect is small, and the repulsion and dispersion terms often may be approximated as spherically symmetrical. One special model for this type of molecule is described in Section 82, but no simple general expression is available.

When highly polar molecules are considered, the dependence on orientation may no longer be neglected. It appears, however, that the asymmetry may be confined to the orientation effect in many cases. A useful potential function would then be

$$\begin{aligned} u &= \lambda r^{-n} - Cr^{-6} - \mu^2 r^{-3} g(\theta_1, \theta_2, \varphi_1, \varphi_2) \\ g &= 2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos(\varphi_2 - \varphi_1) \end{aligned} \quad (74.8)$$

where the angle variables are those of Equation (70.1). Here  $\mu$  is the permanent dipole moment and  $C$  includes *both* induction and dispersion effects. The application of this equation to polar gases is described in Section 83.

**(75) Additivity of Intermolecular Forces:** Although knowledge of the interactions between isolated pairs of molecules is sufficient to deal with the properties of dilute gases, it does not necessarily suffice for the treatment of denser gases or of condensed phases, in which simultaneous interactions among clusters of three or more molecules are predominant. It then becomes necessary to ask whether the intermolecular forces are additive. For example, if we consider three helium atoms quite close to each other, is their mutual potential energy correctly found by simply adding up the three pair-wise interaction energies, as calculated, for example, from Equation (74.7)? More generally, we wish to know whether the total potential energy  $U$  of the entire gas can be expressed as a sum,

$$U = \sum_{i>j} u_{ij} \quad (75.1)$$

taken over all the  $\frac{1}{2}N(N-1)$  possible pair-wise interactions of  $N$  molecules. If the answer is in the affirmative, the general theory of gases is much more simply carried through, and no additional forces need be considered. In this section, the theoretical evidence concerning this question is briefly described.

It appears that for chemically stable substances, such as the rare gases, hydrogen, nitrogen, methane, and the like, the assumption of additivity (while not exact) is nearly valid.<sup>1</sup> This is in good accord with most of the observed properties of such substances.

Coulomb's law for a system of point charges is itself additive, but this is not necessarily true after the averages over the electronic motion have been taken. Each of the effects of Sections 70 to 73 may be considered in turn. The orientation energy of Equation (70.1) is additive if each pair-wise interaction is expressed in terms of all the orientation variables, but this is no longer true of the average value of Equation (70.3). The induction effect is in general not additive, and is virtually absent in cubic crystals, where any one molecule is symmetrically surrounded by others whose fields largely cancel. In dilute gases, where the spatial distribution of the molecules is almost random, the induction effect approaches additivity; but in any case we have seen that this term is generally small.

The second-order dispersion effect was shown by London to be completely additive, irrespective of the spatial distribution of the molecules. This may be regarded as due to the complete lack of phase relations between the fields due to the virtual oscillators in different molecules, just as for light waves from different sources. When the dipole-dipole interaction terms are calculated for a system of three molecules to the *third* order of perturbation energy, a new non-additive term appears,<sup>2</sup> given approximately by

$$u_3 = \frac{9h\nu_0\alpha^3(1 + 3 \cos \gamma_1 \cos \gamma_2 \cos \gamma_3)}{16r_{12}^3 r_{23}^3 r_{13}^3} \quad (75.2)$$

where the three molecular centers form a triangle with sides  $r_{12}$ ,  $r_{23}$ ,  $r_{13}$  and angles  $\gamma_1$ ,  $\gamma_2$ ,  $\gamma_3$ . This term is small; for example, for three argon atoms forming an equilateral triangle at their equilibrium separation of 3.84 Å, Equation (75.2) gives a repulsion only one per cent as large as the second-order attractions found from Equation (72.5). Moreover, its sign varies with the shape of the triangle, being positive for all acute triangles and negative for most obtuse triangles. The attractive forces are thus sufficiently additive for all practical purposes.

First-order exchange forces cannot generally be additive, as is clear from consideration of the valence-bond case. It appears that the departures from additivity are small in the case of repulsions between closed shells, although not negligible for all considerations. Löwdin<sup>3</sup> has shown that non-additive forces exist in alkali halide crystals, and that these play important roles in determining certain of the elastic constants of such crystals. It may also be pointed out

<sup>1</sup> An obvious case of non-additivity is NO<sub>2</sub>, which dimerizes readily to N<sub>2</sub>O<sub>4</sub> but forms no detectable higher polymers.

<sup>2</sup> B. M. Axilrod and E. Teller, *J. Chem. Phys.*, 11, 299 (1943); B. M. Axilrod, *J. Chem. Phys.*, 17, 1349 (1949).

<sup>3</sup> P.-O. Löwdin, *J. Chem. Phys.*, 18, 365 (1950).

that, although the *total* potential energies of crystalline monatomic non-metals and of alkali halides can be very satisfactorily calculated on the assumption of complete additivity, the *differences* between the values for two different lattice types cannot be explained without introducing many-body forces.<sup>4</sup> Thus, while the non-additive terms definitely exist, they contribute only a small part of the total potential energy, and are not likely to be important in determining the properties of amorphous phases. To give a numerical example, we have considered the case of three helium atoms, and found<sup>5</sup> a non-additive first-order exchange energy which is less than half a per cent of the additive terms at all interatomic distances of practical importance. We shall therefore regard the forces as additive in discussing the behavior of gases.

(76) **Deduction of Intermolecular Force Constants from Experiment:** In later sections we shall discuss in some detail the methods of obtaining potential energy constants, such as those of Equation (74.2) or (74.5), from the compressibilities or Joule-Thomson coefficients of gases. Here we mention briefly the other important experimental sources of such information.

The thermodynamic properties of liquids, though obviously intimately related to the intermolecular forces, cannot be used for precise calculations in the absence of a rigorous kinetic or statistical-mechanical theory of the liquid state. However, an approximate free-volume theory of liquids, as developed by Lennard-Jones and Devonshire,<sup>1</sup> may be employed to derive the constants  $\epsilon$  and  $\sigma$  or  $r_0$  of the Lennard-Jones potential energy, Equation (74.3) or (74.4), from liquid densities and vapor-pressures, at least for spherically symmetrical molecules.

The thermodynamic properties of monatomic crystals, extrapolated to the absolute zero of temperature, can be more precisely utilized.<sup>2</sup> If every atom is located at an equilibrium position (i.e., on a lattice point), the distances between all pairs of atoms can be expressed in terms of the separation  $a$  of two nearest neighbors. If the forces are additive, as in Equation (75.1), the total potential energy  $U$  of the crystal can then be summed and expressed as a function of  $a$  and of the parameters of the pair-wise interaction energy  $u$ . The rare gases, nitrogen, and methane all crystallize in the face-centered cubic form, and for this case, with the special Lennard-Jones potential of Equation (74.4), the potential energy of a crystal of  $N$  atoms is found to be

$$U(a) = \frac{N\epsilon}{2} \left[ 12.132 \left( \frac{r_0}{a} \right)^{12} - 2(14.454) \left( \frac{r_0}{a} \right)^6 \right] \quad (76.1)$$

<sup>4</sup> For example, with additive forces the crystal CsCl is predicted to be stable in the face-centered form at ordinary pressures and temperatures, contrary to experimental fact; and solid argon (experimentally always face-centered cubic) is predicted to be equally stable in the hexagonal close-packed form.

<sup>5</sup> Unpublished calculations.

<sup>1</sup> J. E. Lennard-Jones and A. F. Devonshire, *Proc. Roy. Soc. (London)*, **A163**, 53 (1937); **165**, 1 (1938).

<sup>2</sup> For a general account, see R. H. Fowler, *Statistical Mechanics*, 2nd edition (Cambridge, 1936), pp. 312-337.

An atom in a face-centered cubic crystal has 12 nearest neighbors. The numerical factors in this equation, derived by the summations above described, therefore show that the repulsive energy is almost entirely contributed by nearest-neighbor interactions, while about one sixth of the attractive energy is due to interactions involving second or more distant neighbors.

The total energy  $E_0$  of the crystal at the absolute zero is equal to  $U(a)$  plus the zero-point energy of the atoms. The latter has been expressed in terms of the potential-energy constants and of  $a$  by Corner.<sup>3</sup> Hence, since the equilibrium distance  $a_0$  is that value of  $a$  which makes  $E_0$  a minimum, the two relations

$$E_0 = U(a_0) + \sum_i^{3N} (\hbar \nu_i / 2) \quad (76.2)$$

$$(\partial E_0 / \partial a)_{a_0} = 0$$

permit a deduction of the force-constants  $\epsilon$  and  $r_0$ , since the energy of sublimation of the crystal is  $-E_0$  and its density is simply related to  $a_0$ . Some numerical results derived in this way are considered in Section 81. The compressibilities and other elastic constants of crystals are also related to the potential energy, but for these properties, as mentioned in Section 75, the non-additive terms in  $U$  seem to play a more prominent part, and they will not be further considered. The above method is clearly applicable to other functions than that of Lennard-Jones, and has been used for the potential of Equation (74.5).

The transport properties of gases, including viscosity, thermal conductivity, diffusion, and thermal diffusion, are directly related to the intermolecular forces, but the mathematical relations<sup>4</sup> make precise calculations extremely laborious. Recently, however, the necessary numerical integrations have been carried through<sup>5</sup> for the Lennard-Jones potential of Equation (74.3), so that the available sources of potential energy values are considerably increased. As an example, we consider the viscosity-coefficient, for which the theory gives a relation of the form

$$\eta = \frac{(mkT)^{1/2}}{-2} f(kT/\epsilon) \quad (76.3)$$

where  $m$  is the mass of a molecule and  $f(kT/\epsilon)$  is a function which is now tabulated. If the viscosity is known over a sufficiently wide range of temperatures, the potential constants  $\epsilon$  and  $\sigma$  may be obtained by fitting the theoretical function to the observed values. Since the viscosity has been measured with

<sup>3</sup> J. Corner, *Trans. Faraday Soc.*, **35**, 711 (1939).

<sup>4</sup> E. H. Kennard, *Kinetic Theory of Gases* (McGraw-Hill, 1938); S. Chapman and T. G. Cowling, *Mathematical Theory of Non-Uniform Gases* (Cambridge, 1939).

<sup>5</sup> (a) T. Kihara and M. Kotani, *Proc. Phys.-Math. Soc. (Japan)*, **24**, 76 (1942); **25**, 602 (1943); (b) J. O. Hirschfelder, R. B. Bird, and E. L. Spotz, *J. Chem. Phys.*, **16**, 968 (1948); *Chem. Rev.*, **44**, 205 (1949); (c) J. de Boer and J. van Kranendonk, *Physica*, **14**, 442 (1948); (d) J. S. Rowlinson, *J. Chem. Phys.*, **17**, 101 (1949).

considerable accuracy for many gases, reliable Lennard-Jones constants can be obtained in this way; some of the results are given in Section 81.

An approximate treatment of the transport properties, not confined to the Lennard-Jones potential, has been developed by Amdur<sup>6</sup> and applied by him to the rare gases with potentials of the type of Equations (74.5) or (74.7).

The scattering of molecular beams by gases, and the effects of pressure in broadening spectral lines, also yield much information about intermolecular forces, but the results thus far available are of limited applicability for our principal interest, i.e., the equilibrium properties of gases at temperatures not exceeding a few hundred Centigrade degrees.

#### GASES AT MODERATE PRESSURES. THE SECOND VIRIAL COEFFICIENT

(77) **Introduction:** The theory of the equation of state may be developed either from the general theorems of statistical mechanics or by the more specialized and mechanistic methods of kinetic theory. The former approach is the more powerful in dealing with equilibrium states of matter, and has led to the most far-reaching results. Accordingly, the subject is here treated by statistical-mechanical methods.

If the general theory is constructed without the introduction of a specific analytic form for the intermolecular potential energy, the result appears, as will be shown later, in the form of an infinite series:

$$pV/nRT = 1 + (n/V)B(T) + (n/V)^2C(T) + \dots \quad (77.1)$$

As described in Section 3, many investigators have used a polynomial of this form to express their experimental results, using as many terms as necessary for an adequate representation. The theory does much more than merely validate the above form, however, for the functions  $B(T)$ ,  $C(T)$ ,  $\dots$ , are explicitly defined as multiple definite integrals involving the law of intermolecular force. The complexity of almost all of these integrals, even with the simplest reasonable analytic expression for the intermolecular potential, is so great that it has not been possible to express the complete equation of state in closed form in terms of known functions. Thus, closed equations, such as those of van der Waals, Beattie and Bridgeman, or Benedict, Webb and Rubin, have not been obtained rigorously by theoretical methods.

The second virial coefficient,  $B(T)$ , unlike the higher coefficients, is simple enough to yield definite results of great importance, and we shall first consider the equation of state under such conditions that terms in  $C(T)$  or beyond are negligible. In practice, gases at atmospheric pressures usually conform excellently to this criterion.

(78) **The Second Virial Coefficient of a Classical Monatomic Gas:** The most frequent starting-point for treating the properties of a macroscopic system in

<sup>6</sup> I. Amdur, *J. Chem. Phys.*, 16, 190 (1948).

which intermolecular forces play a significant role is the fundamental equation of the canonical ensemble;<sup>1</sup>

$$A = -kT \ln Q \quad (78.1)$$

where  $A$  is the Helmholtz free energy ("work-content"),  $k$  is Boltzmann's constant, and the state sum,

$$Q = \sum_n e^{-E_n/kT} \quad (78.2)$$

goes over all stationary quantum states  $n$  (with energies  $E_n$ ) of the whole system, which is defined to contain a fixed number of particles in a specified volume at the temperature  $T$ . In the limiting case of classical statistics (i.e., at sufficiently high temperatures),  $Q$  is given in terms of the phase integral of Gibbs. For a classical system of  $N$  identical monatomic molecules of mass  $m$ ,

$$Q = \frac{1}{h^{3N} N!} \int \cdots \int e^{-H/kT} dp_1 \cdots dp_{3N} dq_1 \cdots dq_{3N} \quad (78.3)$$

the integrations extending over all attainable values of momenta  $p$  and coordinates  $q$ . Here  $H$  is the Hamiltonian function of the system,

$$H = \sum_{i=1}^{3N} p_i^2/2m + U(q_1, q_2, \cdots, q_{3N}) \quad (78.4)$$

$U$  being the potential energy. The integrations over the momenta are readily effected, with the result

$$Q = \left( \frac{2\pi mkT}{h^2} \right)^{3N/2} \frac{Q_\tau}{N!} \quad (78.5)$$

$$Q_\tau = \int \cdots \int e^{-U/kT} d\tau_1 \cdots d\tau_N$$

In the last expression  $d\tau_i$  is written for the product  $dx_i dy_i dz_i$  involving the coordinates of the  $i$ th molecule. The quantity  $Q_\tau$  is frequently known as the *configuration-integral*. When  $Q_\tau$  is known as a function of volume and temperature, the pressure of the gas is found from the relation

$$p = - \left( \frac{\partial A}{\partial V} \right)_{T,N} = kT \left( \frac{\partial \ln Q}{\partial V} \right)_{T,N} = kT \left( \frac{\partial \ln Q_\tau}{\partial V} \right)_{T,N} \quad (78.6)$$

The perfect gas is easily treated. In this case,  $U$  is everywhere constant (conventionally, zero) inside the container of volume  $V$ , and becomes infinite at the walls. Integration over the coordinates of each molecule then gives a factor  $V$ , so that

$$Q_\tau = V^N; \quad p = kTN/V \quad (78.7)$$

<sup>1</sup> See, for example, J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (John Wiley, 1940), Chap. X.

To make progress in treating a real gas, further specification of  $U$  is necessary, and we assume that it can be written as the sum of the potential energies between all pairs of molecules:

$$U = \sum_{\text{all pairs } i, j} u_{ij} \quad (78.8)$$

It will soon become clear that the second virial coefficient depends only on the pairwise encounters of molecules, so that until higher virial coefficients are considered it will not be necessary to be concerned about the precise validity of this assumption.

The integration of Equation (78.5) can now be carried out in steps, and the treatment presented here<sup>2</sup> is sufficient to give the correct answer as far as the second virial coefficient. We begin by integrating with respect to the coordinates of the  $N$ th molecule while holding those of the other  $(N - 1)$  molecules fixed. To do this, the exponential integrand is factored into the form

$$e^{-U/kT} = e^{-\sum' u_{ij}/kT} e^{-\sum_{i \neq N} u_{iN}/kT} \quad (78.9)$$

where the prime on the first summation-sign denotes omission of all terms involving the  $N$ th molecule. The first factor therefore remains constant during this integration. The integration over the second factor may be written

$$\begin{aligned} \int_{(V)} e^{-\sum u_{iN}/kT} d\tau_N &= \int d\tau_N + \int (e^{-\sum u_{iN}/kT} - 1) d\tau_N \\ &= V + \omega \end{aligned} \quad (78.10)$$

the symbol  $\omega$  denoting the last integral. Since  $\sum u_{iN}$  still depends on the coordinates of *all* the molecules, it may at first seem that the above maneuvers can lead to no useful results.<sup>3</sup> The reassurance comes from the short range of the intermolecular forces, which causes  $\sum u_{iN}$  (and hence the integrand in the formula for  $\omega$ ) to be negligibly small except when the  $N$ th molecule lies quite close to one or more of the other molecules. In Fig. 7, this statement is illustrated by a plot of the function,  $r^2 f(r) = r^2 [e^{-u(r)/kT} - 1]$ , against the intermolecular separation  $r$  at two temperatures, with the Lennard-Jones expression, Equation (74.3), for  $u(r)$ . It is seen that  $r^2 f(r)$  has become very small when  $r$  is two or three times its value at the maximum.

Now, if the gas is sufficiently rare, the possible sets of values of the coordinates of the other  $(N - 1)$  molecules will be such that, as the position of the  $N$ th molecule is varied during integration, it will only rarely<sup>4</sup> come close simultaneously to two or more other molecules. Thus, as the  $N$ th molecule is moved about, the integrand in the formula for  $\omega$  will either be effectively zero,

<sup>2</sup> The procedure here used is that given by J. C. Slater, *Introduction to Chemical Physics* (McGraw-Hill, 1939), pp. 190-194.

<sup>3</sup> If the gas contains charged particles, this method is inapplicable. See the footnote after Equation (78.12).

<sup>4</sup> The chance that a chosen one of the other molecules has a close neighbor can be shown to be of the order of magnitude of  $\omega/V$ , which is small compared to unity when the equation of state can be terminated at the second virial coefficient.



when no other molecules are close, or  $(e^{-u_i N/kT} - 1)$ , when it is close to one other (the  $i$ th) molecule. The integral therefore consists of  $(N - 1)$  contributions, each describing the effect of the interaction of the  $N$ th molecule with one of the others. Since the integrand has sensible values over only such a short range, it is clear that each of these contributions has the same value, say  $\beta$ . Recalling now that the forces between monatomic molecules depend only on their separation  $r$ , we may use relative coordinates and put  $dr = 4\pi r^2 dr$ , thus obtaining

$$\omega = (N - 1)\beta \quad (78.11)$$

where

$$\beta = \int_0^\infty f(r) 4\pi r^2 dr = 4\pi \int_0^\infty [e^{-u(r)/kT} - 1] r^2 dr \quad (78.12)$$

It will be noted that the upper limit of this integral has been taken as infinite, which is justifiable for forces of sufficiently short range. By expanding  $(e^{-u/kT} - 1)$  in series and examining the integral of the first term so obtained, it is found that  $u$  must decrease more rapidly than  $r^{-3}$  if the above integral is to converge. Since the dispersion effect gives a potential whose leading term varies as  $r^{-6}$ , and since valence forces depend even more sharply on  $r$ , there is an ample margin of safety with the presently known types of interatomic forces.<sup>5</sup> Thus  $\beta$  is a function of temperature only.

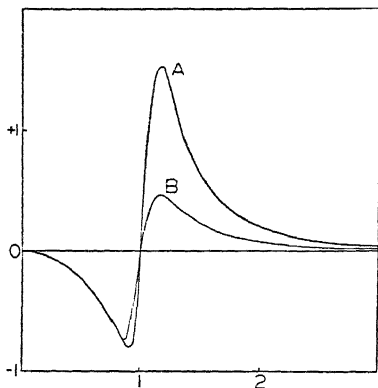


FIG. 7. A function,  $r^2(e^{-u/kT} - 1)$ , related to the second virial coefficient of a non-polar gas. Curves A and B are for  $\epsilon/kT = 0.78$  and  $0.30$ , respectively, corresponding approximately to the critical and Boyle temperatures.

molecules, and yields a factor  $[V + (N - 2)\beta]$ . The complete result is therefore

$$Q_r \simeq \prod_{i=0}^{N-1} (V + i\beta) = V^N \prod_{i=0}^{N-1} \left(1 + \frac{i\beta}{V}\right) \quad (78.13)$$

<sup>5</sup> Coulombic forces between ions, as mentioned earlier, obviously constitute an exception. Newtonian gravitational forces also give a potential varying only as  $r^{-1}$ , but their magnitude is truly negligible, when compared to the electrical forces, for all experimentally attainable gas densities. The problem of gases so rare that gravitational forces are predominant has been of much interest to astronomers. See, for example, A. S. Eddington, *The Internal Constitution of the Stars* (Cambridge, 1926), Chap. IV.

Since the logarithm of  $Q_r$  is needed to find the pressure, and since the above procedure is anyhow valid only as a first approximation, we have (assuming  $i\beta/V \ll 1$  for all  $i$ )

$$\begin{aligned}\ln Q_r &\cong N \ln V + \sum_{i=0}^{N-1} \ln \left( 1 + \frac{i\beta}{V} \right) \\ &\cong N \ln V + \frac{\beta}{V} \sum_{i=0}^{N-1} i + \dots \\ &\cong N \ln V + \frac{N(N-1)}{2} \frac{\beta}{V} + \dots \\ &\cong N \ln V + \frac{N^2\beta}{2V} + \dots\end{aligned}\quad (78.14)$$

Differentiation to obtain the pressure by Equation (78.6) gives

$$pV/NkT = 1 - N\beta/2V + \dots \quad (78.15)$$

A change to molar quantities then shows that the second virial coefficient is

$$B(T) = -N_0\beta/2 = 2\pi N_0 \int_0^\infty (1 - e^{-u(r)/kT}) r^2 dr \quad (78.16)$$

where  $N_0$  is Avogadro's number.

In reviewing the above derivation, it should be recognized that *all* possible binary molecular interactions (but *no* ternary or higher interactions) have been considered. It is true that while integrating over the coordinates of the  $N$ th molecule we considered no configurations in which any two other molecules (say the  $i$ th and the  $j$ th) were close to each other; however, in a subsequent integration the pairwise interaction of these two molecules was fully taken into account. This remark is important because erroneous derivations have sometimes been given.<sup>6</sup>

Although there are several alternative routes<sup>7</sup> to Equation (78.16), space does not permit considering all of them here. However, the discussion would be incomplete without at least a brief mention of the *virial theorem* of Clausius, from which the temperature functions in the equation of state derive their name. For a classical system of monatomic molecules, this theorem<sup>8</sup> may be expressed in the form

$$\langle \Sigma (\frac{1}{2}mv^2) \rangle_N = -\frac{1}{2} \langle \Sigma (\mathbf{F} \cdot \mathbf{R}) \rangle_N \quad (78.17)$$

<sup>6</sup> For a consciously erroneous derivation and an exposition of its fallacy, see J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (John Wiley, 1940), Chap. XII; see also R. H. Fowler, *Statistical Mechanics* (Cambridge, 1936), pp. 240-245.

<sup>7</sup> See R. H. Fowler, *Statistical Mechanics*, 2nd edition (Cambridge, 1936), Chap. IX; also E. H. Kennard, *Kinetic Theory of Gases* (McGraw-Hill, 1938), Chap. V.

<sup>8</sup> For derivations of the virial theorem and its application to the equation of state, see R. H. Fowler, *loc. cit.*, Chap. IX; or J. H. Jeans, *Dynamical Theory of Gases*, 4th edition (Cambridge, 1925), Chap. VI.

In this equation, the left-hand member is simply the time-average kinetic energy of all the particles. The right-hand member, which is the function that Clausius called the *virial*, involves the time-average of the sum over all particles of the scalar product of the net body force  $\mathbf{F}$  on a particle (including that due to the other particles and that due to the external pressure) into its position-vector  $\mathbf{R}$ , referred to any convenient origin of coordinates. The left-hand member is seen to be  $\frac{3}{2}NkT$ . When the virial is analyzed into its components, Equation (78.17) leads to the result

$$pV = NkT - \frac{2\pi N^2}{3V} \int_0^\infty \left( \frac{du}{dr} \right) g(r) r^3 dr \quad (78.18)$$

In this expression,  $u$  is the potential energy between a pair of molecules, as before, and  $g(r)$  is the pair distribution-function, so defined that the number of particles contained in a spherical shell of thickness  $dr$  at a distance  $r$  from any chosen particle is given by  $(N/V)g(r)4\pi r^2 dr$ . This result is valid for classical systems of any sort, but without specification of  $g(r)$  it is of little use. The first approximation to  $g(r)$ , adequate for dilute gases, is simply the Boltzmann factor,  $e^{-u/kT}$ . Substituting this approximation into Equation (78.18), we have an equation terminating with the second virial coefficient, which is then given by

$$B(T) = - \frac{2\pi N_0}{3kT} \int_0^\infty \left( \frac{du}{dr} \right) e^{-u/kT} r^3 dr \quad (78.19)$$

This is exactly equivalent to Equation (78.16), as can be verified by integrating the latter by parts.

Equation (78.16) for the second virial coefficient, or its equivalent, Equation (78.19), may be regarded as an integral equation for the intermolecular energy  $u(r)$ , and it is of a type which has been well studied by mathematicians.<sup>9</sup> Thus, in principle, if  $B(T)$  were known from experimental measurements with sufficient precision, it would be possible to invert Equation (78.16) and obtain the function  $u(r)$ . Unfortunately, the "sufficient precision" required for a unique answer is far beyond that at our disposal, since knowledge of  $B(T)$  and *all* its derivatives at *all* finite temperatures is demanded. We are therefore reduced to the procedure of *assuming* analytical forms for  $u(r)$ , performing the integration required by Equation (78.16), and then comparing the result with experimental  $B(T)$  values to test the validity of the assumed form and to evaluate the constants numerically. Fortunately, the existing theory of intermolecular forces, as we have seen, offers rather definite guidance as to the proper form of the function  $u(r)$ , so that its construction to a good approximation is possible in many cases. The results of such calculations are described later.

(79) **Quantum Theory of the Second Virial Coefficient of a Monatomic Gas:** The considerations of the preceding section were based on the classical approxi-

<sup>9</sup> R. E. A. C. Paley and N. Wiener, *Am. Math. Soc. Coll. Pub. XIX* (1934), Chap. III.

mation, Equation (78.3), to the rigorous quantum-mechanical formula of Equation (78.2) for the state sum. The classical formula is only asymptotically valid at high temperatures, and it is pertinent to inquire whether appreciable errors are introduced by its use. It turns out that almost all of the common gases display no significant departures from classical behavior under attainable conditions (i.e., until the vapor-pressure of their liquid or solid forms becomes very low), but for the four lowest-boiling substances—helium, hydrogen, deuterium, and neon—quantum effects are by no means negligible. Accordingly, the quantum-statistical theory of  $B(T)$  is briefly considered here.

There are two respects in which the classical statistical formula requires amendment. The first, and most important for our problem, is due to the restriction of the possible energies of any finite system to values corresponding to the stationary states; the state sum of Equation (78.2) cannot be rigorously replaced by the phase integral of Equation (78.3), and the probability of a given configuration is not exactly proportional to  $e^{-U/kT}$ . The second modification is due to the exclusion principle, which limits the allowed stationary states to those whose wave functions possess the proper symmetry character with respect to permutations of the coordinates of identical atoms. Thus, when the individual molecules contain even or odd numbers of fundamental particles (nucleons plus electrons), the system obeys Bose-Einstein or Fermi-Dirac statistics, respectively.<sup>1</sup> Fortunately, the approximation of first regarding the molecules as distinguishable and later correcting for their identity through division of the state sum by  $N!$ , as in Equation (78.3), is sufficiently valid for most purposes; the correction to  $B(T)$  thus neglected is relatively unimportant even for helium, being simply the second term in the equation of state for the weakly degenerate Bose-Einstein perfect gas.<sup>2</sup>

A fruitful attack on the quantum-statistical problem was initiated by Slater,<sup>3</sup> who showed how the sum over states, Equation (78.2), could be transformed into an integral over the coordinates of the molecules. Let  $\psi_n(q_1 \cdots q_{3N})$  be the normalized wave-function (excluding the time) for the  $n$ th stationary state of the entire gas. Then the differential quantity,  $|\psi_n|^2 d\tau_1 \cdots d\tau_N$ , gives the probability that the coordinates of the system, when in the  $n$ th state, lie in the hyper-volume element  $d\tau_1 \cdots d\tau_N$ . If the wave-function is normalized, the integral of this probability over all available configuration-space is unity. Now also, in the canonical distribution, the probability that the system is in the  $n$ th state is given by  $e^{-E_n/kT}/Q$ . It follows that the expression

$$\sum_n |\psi_n|^2 e^{-E_n/kT} d\tau_1 \cdots d\tau_N / Q \quad (79.1)$$

is the probability that the coordinates of the system, when it is in equilibrium with surroundings at temperature  $T$ , lie in  $d\tau_1 \cdots d\tau_N$ . Since the integral of

<sup>1</sup> See J. G. Aston, Volume I of this treatise, Chap. IV.

<sup>2</sup> Aston, *loc. cit.*, p. 544, Equation (26, 27).

<sup>3</sup> J. C. Slater, *Phys. Rev.*, **38**, 237 (1931).

this expression must be unity, we have the identity

$$\int \dots \int \sum_n |\psi_n|^2 e^{-E_n/kT} d\tau_1 \dots d\tau_N \quad (79.2)$$

so that the state sum has been expressed as a configuration integral.

For deriving the second virial coefficient,<sup>4</sup> it is not necessary to apply Equation (79.2) to the entire gas; it is sufficient to consider a system containing just two molecules, since  $B(T)$  depends only on binary interactions. To justify this procedure, we here merely remark that it is seen *a posteriori* to suffice for the classical calculation of the previous section. It can be demonstrated rigorously by considering the separability of the Schrödinger equation for systems with non-interacting parts. Referring to Equation (78.13), we may therefore expect the volume-dependent factor of  $Q$  for a two-particle system to have the form  $V(V + \beta)$ , but that the quantum-mechanical recipe for  $\beta$  will be different from the classical one of Equation (78.12).

The problem is then that of two particles of mass  $m$  in a volume  $V$ , interacting according to a potential energy  $u(r)$ . The motion of the center of mass is separable from the internal motion, as usual, and its contribution to the state sum may be immediately factored out. Since free translational modes yield classical partition-functions at all attainable temperatures, it is at once permissible to write

$$Q = [2\pi(2m)kT/h^2]^{3/2} V Q_r \quad (79.3)$$

with

$$Q_r = \sum_r e^{-E_r/kT} = \int \sum_r |\psi_r|^2 e^{-E_r/kT} d\tau_r \quad (79.4)$$

In this equation, the subscript  $r$  denotes states of the *relative* motion of the two molecules.

The relative motion must now be considered further, and this is equivalent<sup>5</sup> to that of a single particle with the reduced mass,  $\mu = m/2$ , moving in the field  $u(r)$  and within  $V$ . The wave-functions and energies are therefore given by the solutions of the Schrödinger equation

$$H\psi_r = -\frac{\hbar^2}{8\pi^2\mu} \nabla^2 \psi_r + u(r)\psi_r = E_r \psi_r \quad (79.5)$$

Since the potential field depends only on  $r$ , the equation is separable in spherical coordinates, and the angular functions will be spherical harmonics. Hence, the integration over the angle variables in Equation (79.4) is always the same, and need not be further considered. In the following development we therefore regard  $\psi_r$  as the normalized *radial* part of the wave-function and replace  $d\tau_r$  by  $4\pi r^2 dr$ .

<sup>4</sup> The development here essentially follows that of G. E. Uhlenbeck and E. Beth, *Physica*, 3, 729 (1936); *ibid.*, 4, 915 (1937).

<sup>5</sup> See, for example, the treatment of the hydrogen atom by S. Dushman, Vol. I, Chap. 2.

Two special cases of the problem can immediately be solved, and aid in later steps:

(1) If classical mechanics were valid,

$$Q_r(\text{class.}) = \frac{1}{2}(2\pi\mu kT/h^2)^{3/2} \int_{(V)} 4\pi r^2 e^{-u/kT} dr \quad (79.6)$$

which would lead to Equation (78.12).

(2) If  $u(r)$  were everywhere zero (perfect gas), the relative motion would also be a free translation, giving

$$Q_r^0 = \frac{1}{2}(2\pi\mu kT/h^2)^{3/2} V \quad (79.7)$$

In each of these expressions, the initial factor  $\frac{1}{2}$  is required by the exclusion principle, since the two atoms are identical.

It is now convenient to rewrite Equation (79.4) as follows:

$$Q_r = \frac{1}{2}(2\pi\mu kT/h^2)^{3/2} \int_{(V)} 4\pi r^2 S(r) dr$$

$$S(r) = \sum |\varphi_r|^2 e^{-E_r/kT} \quad (79.8)$$

$$|\varphi_r|^2 = 2(h^2/2\pi\mu kT)^{3/2} |\psi_r|$$

The function  $S(r)$  has been called<sup>6</sup> the "Slater sum," and comparison of Equations (79.6) and (79.8) shows that its classical limit is simply  $e^{-u/kT}$ . The functions  $\varphi_r$  are just the old wave-functions normalized differently. Since the wave-functions must reduce to those of a free particle at large distances, where  $u$  becomes negligible,  $S(r)$  approaches unity for large  $r$ .

The integral of Equation (79.8) can now be treated as in the classical case:

$$\int_{(V)} S(r) d\tau_r \quad V + \beta = V + \int_0^\infty [S(r) - 1] d\tau_r \quad (79.9)$$

Hence, the second virial coefficient is found to be

$$B(T) = -N_0\beta/2 = 2\pi N_0 \int_0^\infty r^2 [1 - S(r)] dr \quad (79.10)$$

and the classical formula, Equation (78.16), represents a limiting case of this result.

For a completely rigorous calculation of  $B(T)$ , the Slater sum can be evaluated only by finding the solutions of the wave equation (79.5). Unfortunately, this is possible only by tedious numerical integrations with potential functions such as those of Equations (74.2) and (74.5). For the special methods that have been employed in carrying out such detailed calculations for helium, the reader is referred to the original papers.<sup>7</sup>

<sup>6</sup> Uhlenbeck and Beth, *loc. cit.*

<sup>7</sup> Uhlenbeck and Beth, *loc. cit.*; L. Gropper, *Phys. Rev.*, **51**, 1108 (1937); H. S. W. Massey and R. A. Buckingham, *Proc. Roy. Soc. (London)*, **A168**, 378 (1938); J. de Boer and A. Michels, *Physica*, **6**, 409 (1939); R. A. Buckingham, Hamilton, and H. S. W. Massey, *Proc. Roy. Soc. (London)*, **A179**, 103 (1941).

When the deviations from classical statistics are slight, as for most gases, it is not necessary to solve the Schrödinger equation. In this case, the state sum can be expanded<sup>8</sup> as a series in even powers of Planck's constant  $h$ , the leading term of the series being the classical approximation. The succeeding terms require knowledge of  $u(r)$ , but not of the wave-functions. Applying this method to the present problem, Uhlenbeck and Beth derived the result

$$B(T) = B(\text{classical}) + B^{(1)} + B^{(2)} + \dots \quad (79.11)$$

Here we give only the formula for the first correction-term, which is usually sufficient:

$$B^{(1)} = \frac{h^2 N_0}{24\pi m (kT)^3} \int_0^\infty r^2 \left( \frac{du}{dr} \right)^2 e^{-u/kT} dr \quad (79.12)$$

The higher terms depend also on higher derivatives of the potential. Numerical values of  $B^{(1)}$  for some of the common gases will be considered in a later paragraph.

One further development of Equation (79.10) is illuminating. The quantum states of the relative motion of the two particles fall into two classes: those with positive energy levels (referred to the conventional choice of a zero potential energy for isolated particles), and those with negative levels. The former are virtually continuous in a large volume, while the latter form a finite set of discrete levels corresponding to the rotational and vibrational states of a (not very stable) diatomic molecule. The wave-functions of these molecular states fall to negligible values at large distances, while those of the positive continuum behave asymptotically like those of a free particle. It is therefore possible to split the Slater sum into two parts,

$$S(r) = S_{\text{cont.}}(r) + S_{\text{discr.}}(r) \quad (79.13)$$

of which the former goes asymptotically to unity and the latter to zero. Hence Equation (79.10) becomes

$$B(T) = 2\pi N_0 \int_0^\infty r^2 [1 - S_{\text{cont.}}(r)] dr - 2\pi N_0 \int_0^\infty r^2 S_{\text{discr.}}(r) dr \quad (79.14)$$

By referring to Equation (79.8), it is seen that the second term, contributed by the "molecular" states, can be written

$$B_{\text{discr.}} = - N_0 (h^2 / 2\pi \mu kT)^{3/2} \sum_{\text{discr.}} e^{-E_r/kT} \quad (79.15)$$

Now it can easily be shown that this is simply the negative of the equilibrium-constant governing the formation of the diatomic molecules from the atoms, according to the statistical formulae for perfect gases.<sup>9</sup> Letting  $n_1$  and  $n_2$

<sup>8</sup> F. Bloch, *Z. Physik*, **74**, 295 (1932); E. P. Wigner, *Phys. Rev.*, **40**, 749 (1932); J. G. Kirkwood, *Phys. Rev.*, **44**, 31 (1933).

<sup>9</sup> This treatise, Vol. I, Chaps. III and IV.

represent the moles of single and double molecules, and  $Q_1$  and  $Q_2$  their respective partition-functions, we have

$$\begin{aligned}
 K &= (n_2/V)/(n_1/V)^2 = N_0 V Q_2 / Q_1^2 \\
 &= \frac{N_0 V (2\pi \cdot 2mkT/h^2)^{3/2} V \sum_{\text{discr.}} e^{-E_r/kT}}{[(2\pi mkT/h^2)^{3/2} V]^2} \\
 &= N_0 (h^2/2\pi\mu kT)^{3/2} \sum_{\text{discr.}} e^{-E_r/kT}
 \end{aligned} \tag{79.16}$$

At sufficiently low temperatures, such that the contribution of the continuum is small compared to  $B_{\text{discr.}}$ , it may be profitable to take advantage of this identity and regard  $-B(T)$  as a dimerization constant. This question is later considered in more detail.

The approximate number,  $n$ , of vibrational states accessible to such diatomic molecules can be found by applying the Wilson-Sommerfeld rule of the old quantum theory.<sup>10</sup> Using the Lennard-Jones potential of Equation (74.3), we obtain

$$n \sim \frac{1}{h} \int_{\sigma}^{\infty} (-2mu)^{1/2} dr = 0.045\sigma(M\epsilon/k)^{1/2} \tag{79.17}$$

where  $\sigma$  is in Å,  $M$  the molecular weight of the monomer in grams, and  $\epsilon/k$  is in Kelvin degrees. With the numerical values of the potential constants  $\sigma$  and  $\epsilon$  listed in Section 81, the values given in Table VIII are found. It is seen

TABLE VIII  
NUMBERS OF DISCRETE VIBRATIONAL ENERGY LEVELS IN DOUBLE  
MOLECULES OF CERTAIN GASES

<i>Gas</i>	<i>Number of Vibrational States</i>
He.....	0 or 1
H <sub>2</sub> , D <sub>2</sub> .....	1 or 2
Ne.....	3 or 4
N <sub>2</sub> .....	8
A.....	10
Kr.....	18
Xe.....	30

that all but the four lightest gases have an appreciable number of levels. Hydrogen and nitrogen, though diatomic gases, have been included for reasons to be given later. For helium, as mentioned earlier, the Schrödinger equation has actually been solved numerically with several different potential functions. Some of these calculations led to one discrete level, lying only slightly below zero, while in others no level was found. Since the classical formula must be regained when the number of levels becomes very large, the order of the gases in Table VIII is that of decreasing importance of the quantum corrections.

<sup>10</sup> See Dushman, this Treatise, Vol. I, Chap. 2.



(80) **Diatomic and Polyatomic Gases:** The rotations of molecules and their intramolecular vibrations are influenced by the presence of neighboring molecules. This statement is almost self-evident for rotations, since the intermolecular forces in general depend not only on the distances between centers of mass but also on orientations. The vibrational modes are not very much affected, as is demonstrated by the fact that the vibrational frequencies deduced from the infra-red absorption spectra of liquids are usually nearly the same as for the corresponding gases. Physically, this means that the intermolecular forces are small compared to the intramolecular valence forces which govern the vibrational motions. To a good approximation, therefore, the contribution of the intramolecular vibrations to the state sum will be dependent only on temperature, and need not be considered in deducing the equation of state.

The amplitudes of the intramolecular vibrations are small in most molecules, and the mean values of interatomic distances and bond angles vary only very slowly with temperature. Hence it is usually adequate to regard the molecules as rigid when considering the gas imperfections.<sup>1</sup> When the rotational motions of these rigid molecules are effectively classical, as will be true in most cases,<sup>2</sup> the analysis is readily completed. For illustration, we consider a gas of  $N$  diatomic molecules of mass  $m$ , mean moment of inertia  $I$ , and vibrational frequency  $\nu$ . With the approximations just discussed, the state sum becomes

$$Q = \left( \frac{2\pi mkT}{h^2} \right)^{\frac{3N}{2}} \left( \frac{2\pi IkT}{h^2} \right)^N (1 - e^{-h\nu/kT})^{-N} \frac{Q_r}{N!}$$

with

$$Q_r = \int \cdots \int_{(V)} e^{-U/kT} d\tau_1 \cdots d\tau_N \quad (80.1)$$

and

$$d\tau_i = \sin \theta_i d\theta_i d\varphi_i dx_i dy_i dz_i$$

where  $\theta_i$  and  $\varphi_i$  are angles specifying the orientation of the  $i$ th molecule and  $x_i, y_i, z_i$  locate its center of mass. The decomposition of  $Q_r$  then follows as in Section 78, with the result <sup>3</sup>

$$B(T) = \frac{N_0}{4} \int_0^\infty \int_0^\pi \int_0^\pi \int_0^{2\pi} (1 - e^{-u/kT}) r^2 \sin \theta_1 \sin \theta_2 dr d\theta_1 d\theta_2 d\varphi \quad (80.2)$$

where  $r$  is the distance between the centers of mass,  $\theta_1$  and  $\theta_2$  are the latitudes of the two molecular axes (with respect to an axis along  $r$ ), and  $\varphi (= \varphi_2 - \varphi_1)$  is

<sup>1</sup> Molecules with internal rotations will immediately be recognized as exceptions to this statement. For example, the molecules of *n*-heptane or of ethylene chloride could not safely be treated as rigid. However, in some cases (e.g., ethane, isobutane, tetramethylmethane), the internal rotations might have negligible effects on the intermolecular potential, so that a rigid model would suffice.

<sup>2</sup> The exceptions will be molecules with small moments of inertia, i.e., hydrides.

<sup>3</sup> The quantum correction for this case has been given by J. G. Kirkwood, *J. Chem. Phys.*, 1, 597 (1933).

the difference in their longitudes. When  $u$  depends only on  $r$ , the integration over  $\theta_1$ ,  $\theta_2$ , and  $\varphi$  can be effected at once, and Equation (78.16) is recovered. When the molecules are non-linear, two additional angular variables are needed to specify the orientation, but the extension of Equation (80.2) to this case is obvious and need not be given explicitly here.

Since it was stated in Section 70 that the potential energy between two dipoles varies as  $r^{-3}$  for fixed orientations, the convergence of the integral of Equation (80.2) might be questioned when  $u$  contains such a term. However, it has also been pointed out that the average value over all orientations of such a contribution to  $u$  (and, indeed, of all its odd powers) is zero. Hence, if  $e^{-u/kT}$  is expanded and if the integrations over the angles are performed first, no difficulties of convergence arise. The same is true of the interactions due to permanent quadrupoles or higher multipoles.

In the sections immediately following, special integrations of the above-derived formal expressions for  $B(T)$  will be described and compared with the experimental results.

**(81) Second Virial Coefficients and Intermolecular Forces; Spherical and Quasi-Spherical Molecules:** The deduction of intermolecular potential energies from the experimental second virial coefficients is described in this and the next several sections, for several types of molecules. As already pointed out, the only possible procedure at present is to integrate the appropriate formal expression for  $B(T)$  (for example, Equation [78.16]) with a physically reasonable and mathematically convenient form for the intermolecular potential energy,  $u$ , such as one of those cited in Section 74; the parameters in the chosen expression for  $u$  are then obtained by fitting the integrated result to the experimental  $B(T)$  curve. Low-pressure Joule-Thomson coefficients, related to the second virial coefficient by the thermodynamic formula (3.8), have also been used for this purpose.

It is not possible here to describe fully the historical development of this type of investigation. The earliest result deserving attention is that of Keesom,<sup>1</sup> who used the intermolecular field of Equation (74.1). With the attractive field proportional to  $r^{-6}$ , use of this potential in Equation (78.16) gives

$$B(T)/b = 1 - \sum (\epsilon/kT)^n/n!(2n-1) \quad (81.1)$$

with

$$b = 2\pi N_0 \sigma^3/3$$

The relation of this expression to the constants  $b$  and  $a$  in the equations of state of van der Waals and Dieterici has already been given in Equations (3.13) and (3.14). These equations and that of Keyes, Equation (5.5), correspond to retention of only the first term of the sum in Equation (81.1). The Berthelot equation corresponds to representing the sum by its second term only, while

<sup>1</sup> W. H. Keesom, *Comm. Phys. Lab. Leiden, Suppl.*, 24B, 32 (1912).

those of Beattie and Bridgeman and of Benedict, Webb, and Rubin keep the linear and cubic terms in  $T^{-1}$ ; see Sections 4 and 5. Except for helium and hydrogen, Equation (81.1) can give a fair representation of the experimental results for spherical molecules, but the intermolecular potential so derived is scarcely convincing.

The modern phase of this subject began in 1924, when Lennard-Jones<sup>2</sup> evaluated  $B(T)$  with the double reciprocal potential of Equation (74.2). At that time, neither of the exponents of  $r$  in Equation (74.2) could be specified on theoretical grounds, and the experimental results were insufficient to fix them. After the theory of dispersion forces was developed, the attractive field could be written as  $Cr^{-6}$ , but a unique index for the repulsion was still not indicated, equally good agreement being obtainable<sup>3</sup> with values of  $s$  between 9 and 14. In recent years, the choice  $n = 12$  has almost always been made, for reasons of mathematical convenience, and we give the results only for this case, corresponding to Equations (74.3) or (74.4). With the classical Equation (78.16), there is obtained

$$B(T)/\beta = y^{1/2} \sum_{n=0}^{\infty} c_n y^n$$

where

$$c_n = -1' \left( \frac{2n-1}{4} \right) / n! 4$$

$$y = 2(\epsilon/kT)^{1/2} \quad (81.2)$$

$$\beta = 2\pi N_0 \sigma^3 / 3 = 2^{1/2} \pi N_0 r_0^3 / 3$$

As mentioned in Section 3, this expression gives the maximum in  $B(T)$  required for helium, neon, and hydrogen, and fits almost all the experimental results for spherical molecules excellently. Tables of the Lennard-Jones function for the second virial coefficient<sup>4</sup> and of the related function for the low-pressure Joule-Thomson coefficient<sup>5</sup> have been published, and the approximate equations (3.15) and (3.16) describe the former over a considerable range of temperatures. Still another empirical equation,<sup>6</sup> which describes the theoretical function to within five per cent at all temperatures above half the critical temperature, is

$$B/\beta = \left( \frac{\epsilon}{kT} \right)^{1/6} \left[ 1 - 3.477 \left( \frac{\epsilon}{kT} \right) + 0.333 \left( \frac{\epsilon}{kT} \right)^2 - 0.394 \left( \frac{\epsilon}{kT} \right)^3 \right] \quad (81.3)$$

<sup>2</sup> J. E. Lennard-Jones, *Proc. Roy. Soc. (London)*, **A106**, 463 (1924).

<sup>3</sup> J. E. Lennard-Jones, *Proc. Phys. Soc. (London)*, **43**, 461 (1931); R. H. Fowler, *Statistical Mechanics*, 2nd edition (Cambridge, 1936), Chap. X.

<sup>4</sup> W. H. Stockmayer and J. A. Beattie, *J. Chem. Phys.*, **10**, 476 (1942); J. O. Hirschfelder, F. T. McClure, and I. F. Weeks, *ibid.*, **10**, 201 (1942).

<sup>5</sup> J. O. Hirschfelder, R. H. Ewell, and J. R. Roebuck, *J. Chem. Phys.*, **6**, 205 (1938).

<sup>6</sup> G. Scatchard, private communication.

Graphical methods for accurately fitting Equation (81.2) to the experimental curves have been described by Lennard-Jones<sup>7</sup> and by Buckingham.<sup>8</sup> An extremely simple method, which yields good results in most cases, is based on the approximation of Equation (3.16), according to which a plot of  $BT^{1/4}$  against  $T^{-1}$  should yield a straight line, with a slope  $-3.602\beta(\epsilon/k)^{5/4}$ , and an intercept  $1.064\beta(\epsilon/k)^{1/4}$  on the  $BT^{1/4}$  axis at infinite temperature. In Fig. 8, theoretical values of  $(kT/\epsilon)^{1/4}B/\beta$  derived from Equation (81.2) are plotted against  $(\epsilon/kT)$ . It is seen that a straight line reproduces the theoretical function adequately in the range of values of  $\epsilon/kT$  between 0.2 and 1.0, corresponding to a temperature-range from well below the critical temperature to about three halves the Boyle temperature,  $T_B$ . When the Boyle temperature has been experimentally determined, the parameter  $\epsilon$  is easily found, since the zero of Equation (81.2) is given by

$$\epsilon/kT_B = 0.2924 \quad (81.4)$$

The approximate Equation (3.16) gives 0.295.

Before discussing the comparison of Equation (81.2) with experiment, it is necessary to digress briefly in order to consider quantum corrections. As shown in Section 79, the classical formula for  $B(T)$  requires amendment at lower temperatures, especially for the lighter gases. The correction terms  $B^{(1)}$  and  $B^{(2)}$  of Equation (79.11), of which the former has been given in Equation (79.12), have been evaluated with the Lennard-Jones potential by de Boer and Michels.<sup>9</sup> For most gases, a knowledge of  $B^{(1)}$  is sufficient, and the results of de Boer and Michels can be approximately<sup>10</sup> represented by the empirical equation

$$B^{(1)} \cong \frac{56\sigma}{M(\epsilon/k)} \left( \frac{\epsilon}{kT} \right) \left( 1 + 14 \frac{\epsilon}{kT} \right) \text{ cm}^3/\text{mole} \quad (81.5)$$

where  $\sigma$  is in Å,  $M$  is the molecular weight in grams, and  $\epsilon/k$  is in Kelvin degrees. To illustrate the order of magnitude of the quantum correction, Table IX gives values of the classical contribution, from Equation (81.2), and of  $B^{(1)}$ , as calculated by Equation (81.5), for a few gases at  $\epsilon/kT = 0.8$  and 0.4, corresponding roughly, for the heavier gases, to the critical temperature and to twice its value, respectively. The actual Kelvin temperatures are given for each gas in the table, which was constructed with values of  $\epsilon$  and  $\sigma$  to be given later. The results<sup>11</sup> show that at these temperatures the quantum correction is negligible to within experimental error for nitrogen and heavier gases, rather small for neon, but large for helium and the hydrogen isotopes. For helium,

<sup>7</sup> *Loc. cit.*

<sup>8</sup> R. A. Buckingham, *Proc. Roy. Soc. (London)*, A168, 264 (1938).

<sup>9</sup> J. de Boer and A. Michels, *Physica*, 5, 945 (1938).

<sup>10</sup> This result is obtained from another approximate form, given by Corner, which will be described later.

<sup>11</sup> These figures are not intended to be precise, the purpose being merely to indicate orders of magnitude.

TABLE IX  
INITIAL QUANTUM CORRECTIONS TO SECOND VIRIAL COEFFICIENTS OF  
GASES AT SEVERAL TEMPERATURES<sup>1</sup>  
(All values of  $B$  are in cm<sup>3</sup>/mole)

Gas	$\epsilon/kT = 0.8$			$\epsilon/kT = 0.4$		
	$T$	$B_{\text{class}}$	$B^{(1)}$	$T$	$B_{\text{class}}$	$B^{(1)}$
He.....	12.7°	- 36	+34	25.5°	- 6.4	+9.3
H <sub>2</sub> .....	46°	- 54	+21	92°	- 9.4	+5.8
D <sub>2</sub> .....	46°	- 54	+11	92°	- 9.4	+2.9
Ne.....	44.5°	- 44	+ 2.1	89°	- 7.7	+0.6
N <sub>2</sub> .....	120°	-112	+ 0.8	240°	-19.5	+0.2
A.....	150°	- 86	+ 0.4	300°	-15.0	+0.1
Kr.....	196°	-101	+ 0.15	393°	-17.6	+0.04
Xe.....	272°	-135	+ 0.08	543°	-23.6	+0.02

<sup>1</sup> These figures are not intended to be precise, but to indicate orders of magnitude. They are based on rough values of the potential constants and on the approximate Equation (81.5).

$B^{(1)}$  exceeds the classical contribution, and it is clear that the series development of Equation (79.11) does not converge<sup>12</sup> rapidly enough to be trustworthy for helium at these temperatures, so that a more complete treatment of the quantum effects, based on Equation (79.10), is required.

From Equations (81.5) and (81.2), we may write

$$B_{\text{class.}}^{(1)} - \frac{k}{\sigma^2 M \epsilon} f(\epsilon/kT) \quad (81.6)$$

where  $f$  is a function of  $\epsilon/kT$  only. According to this result, the fractional quantum correction (provided  $B^{(2)}$  and higher terms are negligible), at a given value of the reduced temperature  $kT/\epsilon$ , is proportional to the quantity  $(\sigma^2 M \epsilon)^{-1}$ ; and from Equation (79.17) this is inversely proportional to the square of the number of vibrational energy states of the diatomic "polarization molecule." Thus the order of importance of quantum corrections inferred from Table VIII is confirmed. From the magnitudes of Table IX it may also be concluded that isotope effects on the equation of state should be unobservable except for helium, hydrogen, and possibly neon.

From another point of view, quantum effects will be negligible when the wavelength given by the de Broglie relation,  $\lambda = h/p$ , is small compared to the range of molecular interactions. Since the range of interaction is proportional to  $\sigma$ , the ratio  $\lambda/\sigma$  is a measure of the importance of quantum effects. Now

<sup>12</sup> The terms  $B^{(1)}$ ,  $B^{(2)}$ , ..., alternate in sign. It is interesting to note that at the two temperatures given in Table IX the smoothed experimental values of  $B(T)$  for helium are -15.2 and +0.1 cm<sup>3</sup>/mole, as given by W. H. Keesom, *Helium* (Elsevier, 1942), p. 37, Equation (2.11). Thus the series of Equation (79.11) must converge to a quantum correction of the order of 20 cm<sup>3</sup>/mole at 12.7°K, although  $B^{(1)}$  alone is 34 at this temperature.

the average relative momentum  $p$  of two particles at a temperature  $T$  is classically proportional to  $(\mu kT)^{1/2}$ , and hence to  $(M\epsilon)^{1/2}$  at a given value of  $kT/\epsilon$ . The ratio  $\lambda/\sigma$  therefore is proportional to  $(\sigma^2 M\epsilon)^{-1/2}$ , and it is just the square of this quantity that appears in Equation (81.6) above.

Turning now to the comparison of experimental results with predictions based on the Lennard-Jones potential function, we give in Table X the numerical values of the constants that have been obtained by various investigators. Most of them were derived directly from compressibility data, but in some cases these were reinforced by analysis of low-pressure Joule-Thomson coefficients. The characteristic distances  $\sigma$  and  $r_0$  are of course not independent, obeying the relation  $r_0^6 = 2\sigma^6$ , but both are listed for convenience. As an illustration of the degree to which the Lennard-Jones function reproduces the data, a few experimental points for argon (open circles) and for methane (filled circles) have been plotted in Fig. 8, with the aid of the potential constants of Table X.

Attention is called to the alternative sets of constants given for several of the gases in Table X. For nitrogen and methane, they indicate merely the agreement attained by independent investigators, and differ only because of variations in the values of  $B(T)$  obtained by different experimentalists, or because the data were weighted differently. For helium and hydrogen, the values first given were deduced by de Boer and Michels, who took the quantum corrections into account. The other values, given in parentheses and marked with asterisks, were derived by Buckingham and by Lennard-Jones from the results at higher temperatures only (above 70°K for helium), on the supposition that the quantum corrections were negligible over the range considered. It is clear from the numerical values, especially those of  $\epsilon$ , that this assumption was not fully justified. Empirically, of course, use of the starred values in the classical equation gives adequate representation of the data over the temperature-range considered; this is analogous to the use of fictitious critical constants in the corresponding-states treatment of hydrogen and helium, as described in Section 2. It should be mentioned that the helium potential of

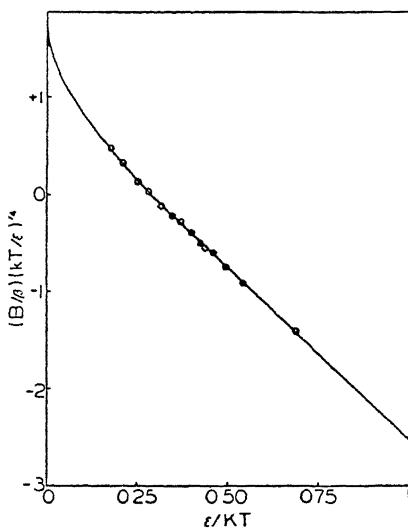


FIG. 8. A function,  $(B/\beta)(kT/\epsilon)^{1/4}$ , related to the second virial coefficient  $B$  for spherical non-polar molecules. Experimental points for argon (open circles) and methane (filled circles) are included, the constants  $\beta$  and  $\epsilon$  for these gases being listed in Table X. Note the linearity of this function for  $\epsilon/kT > 0.2$ .

TABLE X

LENNARD-JONES POTENTIAL ENERGY PARAMETERS DERIVED FROM SECOND VIRIAL COEFFICIENTS AND LOW-PRESSURE JOULE-THOMSON COEFFICIENTS OF GASES

Gas	$\epsilon/k$	$\sigma(\text{\AA})$	$r_0(\text{\AA})$	Reference
He.....	10.2°	2.56	2.88	<i>a</i>
	(6.03°) *	(2.60) *	(2.92) *	<i>b</i>
Ne.....	35.7°	2.74	3.08	<i>b</i>
Ar.....	119°	3.41	3.84	<i>b</i>
Kr.....	172°	3.59	4.03	<i>c</i>
Xe.....	224°	4.06	4.56	<i>c</i>
H <sub>2</sub> .....	37.0°	2.92	3.28	<i>a</i>
	(30.7°) *	(2.92) *	(3.28) *	<i>d</i>
N <sub>2</sub> .....	95.3°	3.65	4.10	<i>e</i>
	95.9°	3.72	4.18	<i>f</i>
CH <sub>4</sub> .....	148°	3.79	4.25	<i>g</i>
	143°	3.81	4.28	<i>f</i>
O <sub>2</sub> .....	118°	3.58	4.02	<i>f</i>
NO.....	131°	3.17	3.57	<i>f</i>
CO <sub>2</sub> .....	185°	4.57	5.13	<i>f</i>
N <sub>2</sub> O.....	189°	4.59	5.15	<i>f</i>

\* These values were derived from the data at higher temperatures, with neglect of all quantum corrections.

<sup>a</sup> J. de Boer and A. Michels, *Physica*, 5, 945 (1938).

<sup>b</sup> R. A. Buckingham, *Proc. Roy. Soc. (London)*, A168, 264 (1938).

<sup>c</sup> J. A. Beattie, R. Barriault, and J. S. Brierley, to be published.

<sup>d</sup> J. E. Lennard-Jones, *Physica*, 4, 941 (1937).

<sup>e</sup> J. Corner, *Trans. Faraday Soc.*, 36, 780 (1940).

<sup>f</sup> J. O. Hirschfelder, F. T. McClure, C. F. Curtiss, and D. W. Osborne, NDRC-A 116; results only quoted by J. O. Hirschfelder, R. B. Bird, and E. L. Spotz, *J. Chem. Phys.*, 16, 968 (1948).

<sup>g</sup> J. Corner, *Proc. Roy. Soc. (London)*, A192, 275 (1948).

de Boer and Michels, obtained from the data at higher temperatures where the quantum corrections are small enough to permit use of Equation (79.11), was subsequently shown by them<sup>13</sup> to give a better fit than the several existing alternative expressions (though by no means a perfect one) at very low temperatures, where numerical calculations based more directly on Equation (79.10) are required.

The diatomic and polyatomic gases included in Table X cannot strictly have intermolecular potentials which depend only on the separation  $r$ , but their second virial coefficients conform well to the Lennard-Jones equation. This is eminently true for hydrogen, nitrogen, and methane; for the last four gases a detailed discussion of the results has not yet become generally available, but from the published experimental results for these substances it may be conjectured that the given constants are somewhat less reliable than for the

<sup>13</sup> J. de Boer and A. Michels, *Physica*, 6, 409 (1939).

other gases listed. The behavior of non-spherical molecules is treated in more detail in subsequent paragraphs. Here we remark only that the constants of Table X must describe the *average* intermolecular energy over all possible orientations of two molecules, and that for the gases listed the deviations from this average are not sufficient to produce measurable anomalies. In other words, the hindrance to molecular rotation caused by asymmetry of the force fields is not very great, so that all orientations are still almost equally probable.

Having found that the potential of Equation (74.3) gives an adequate representation of the experimental second virial coefficients of many gases, we must remind ourselves that we have not necessarily obtained a *unique* solution, and that even if we persist in using a bireciprocal form the index  $n$  of the repulsive energy could be varied over the range from 9 to 14, with appropriate changes in the other constants, with preservation of the agreement. That such variations are possible over a limited range can be readily understood when we recall that a plot of the experimental values of  $BT^{1/4}$  against  $T^{-1}$ , as suggested by Equation (3.16), is actually linear over a large temperature range. This means that we can uniquely determine only *two* constants for the gas, corresponding to the two constants specifying the straight line. Thus, if a potential energy function has the generally correct form and contains *three* adjustable constants (say  $\epsilon$ ,  $\sigma$ , and  $n$  in a Lennard-Jones potential), no unique set of these constants can be obtained from the data. Once one of the constants is fixed, as by arbitrarily choosing  $n = 12$ , the remaining two can be rather precisely specified.

It is therefore necessary to see whether the potential of Equation (74.3), with the constants listed in Table X, can also be used to predict correctly other properties of the substances concerned. This can be done for the heats of sublimation and lattice spacings of the corresponding crystals and for the viscosities of the gases, as mentioned in Section 76. A few potential-constants derived from crystal data and viscosities are collected in Table XI. Crystal calculations for helium and hydrogen are not included because the effects of their large zero-point energies (e.g., about 75 per cent of the lattice energy for solid He) cannot be rigorously calculated. For the same reason, the value of  $\sigma$  deduced for neon is less certain than the other values given. The viscosity results, due to Hirschfelder, Bird, and Spotz,<sup>14</sup> are free from quantum corrections, since the data used were all for temperatures of 80°K and above.<sup>15</sup> It is seen that the agreement among the three sets of potential-constants is fairly good for the rare gases and hydrogen, nitrogen, and methane, the average deviations between any two methods being less than 0.05 Å in  $\sigma$  and less than five per cent in  $\epsilon$ . It is interesting that for nitrogen and hydrogen the crystal data give larger values of  $\epsilon$  and smaller values of  $\sigma$  than those obtained from the second virial coefficients; this is just what would be expected for asymmetrical molecules, which would be frozen into preferred orientations in the solid. Large discrepancies between the viscosity and compressibility results are ap-

<sup>14</sup> J. O. Hirschfelder, R. B. Bird, and E. L. Spotz, *J. Chem. Phys.*, **16**, 968 (1948).

<sup>15</sup> I. Amdur, *J. Chem. Phys.*, **16**, 190 (1948).



parent for oxygen and carbon dioxide; these may also be due to departures from spherical symmetry, or perhaps to the effects of inelastic collisions on the viscosity.

Now, although Table XI gives reassurance that Equation (74.3) is a fair approximation to the intermolecular energy, the differences between the several sets of constants are in most cases too large to be blamed on experimental errors.

TABLE XI  
LENNARD-JONES POTENTIAL ENERGY PARAMETERS DERIVED FROM  
LATTICE ENERGIES AND GAS VISCOSITIES

Substance	From Lattice Energies <sup>a</sup>		From Viscosities <sup>b</sup>	
	$\epsilon/k$	$\sigma(\text{\AA})$	$\epsilon/k$	$\sigma(\text{\AA})$
He.....	—	—	6.0°	2.70
Ne.....	36.6°	2.81 *	35.7°	2.80
Ar.....	118.3°	3.45	124°	3.42
Kr.....	170°	3.60	—	—
Xe.....	230°	3.97	—	—
H <sub>2</sub> .....	—	—	33.3°	2.97
N <sub>2</sub> .....	108°	3.64	91.5°	3.68
CH <sub>4</sub> .....	157°	3.76	137°	3.82
O <sub>2</sub> .....	—	—	113°	3.43
CO <sub>2</sub> .....	—	—	190°	4.00

<sup>a</sup> Calculated by the method of J. Corner, *Trans. Faraday Soc.*, 35, 711 (1939); lattice energies and distances from various sources.

<sup>b</sup> J. O. Hirschfelder, R. B. Bird, and E. L. Spotz, *J. Chem. Phys.*, 16, 968 (1948).

\* This value is less certain than others because the large effect of zero-point energy can be only approximately evaluated.

The discrepancies can be reduced, but not completely removed, by varying the repulsive index  $n$  from its chosen value of 12. The index can be adjusted to give exact agreement between the virial coefficient and *either* the lattice energy  $U_0$  or the lattice distance  $a_0$ , but not both simultaneously. The following figures, for example, were obtained by Corner <sup>16</sup> for neon and argon:

Substance	To fit $a_0$	To fit $U_0$
neon.....	$n = 10.5$	$n = 12.6$
argon.....	$n = 11.0$	$n = 11.8$

Clearly no function of the form of Equation (74.2) can give a perfect description of the intermolecular field, at least as long as the exponent in the attractive energy is kept at the theoretically correct value of 6.

A substantial improvement results from replacing the inverse-power formula for the repulsive energy by the theoretically preferable exponential form, as in Equations (74.5) and (74.6). This is the type of expression first suggested by

<sup>16</sup> J. Corner, *Trans. Faraday Soc.*, 35, 711 (1939).

Slater<sup>17</sup> for helium. Attempts to obtain an analytical expression for  $B(T)$  with this potential have not been successful, but if the numerical constants are known or assumed, numerical or graphical integration is of course possible.<sup>18</sup> The inverse problem, that of determining the potential constants from the virial coefficients, is less readily accomplished, but Buckingham<sup>19</sup> has developed a method making use of the Lennard-Jones formulae in auxiliary fashion. Since Equation (74.5) or (74.6) contains three disposable constants ( $A$ ,  $\rho$ , and  $C$  or  $\epsilon$ ,  $r_0$ , and  $\alpha$ ) it is again impossible to obtain a unique energy function from the gas data alone. For neon and argon, Buckingham chose the constants giving agreement with the observed energies of sublimation, and Corner (*loc. cit.*) later showed that these also predicted lattice distances within 0.01 Å of the observed values. This is far superior to the Lennard-Jones results. For helium, crystal data cannot be safely used, but the large quantum effects on  $B(T)$  at very low temperatures are very sensitive to the exact form of the potential and thus could in principle be used to obtain a rather unique result. Unfortunately, inversion of this problem is hopelessly difficult, and up to now no single expression fitting all the virial coefficients of helium to within experimental error has been published. The Lennard-Jones potential of de Boer and Michels (Table X) seems to give the best over-all fit of the functions thus far examined. The compressibilities of krypton and xenon have only recently been measured,<sup>20</sup> and application of Equation (74.5) to the results has not yet been made. However, Kane<sup>21</sup> has deduced potentials of this form from the crystal parameters of krypton and xenon, for several assumed values of  $\rho$ . We shall not give numerical values of such potential functions here, except for one example. Buckingham's result for neon leads to  $\epsilon/k = 38.5^\circ$ ,  $r_0 = 3.12$  Å,  $\sigma = 2.76$  Å, again showing that the Lennard-Jones figures (Table X) give a fair approximation.

Still another refinement in the potential energy function would be the introduction of a term varying as  $r^{-8}$ , representing the dipole-quadrupole contribution to the dispersion effect. The fourth constant thus introduced cannot be uniquely determined from experimental data, but its ratio to the dipole-dipole dispersion term can be calculated theoretically with sufficient precision. Recently Buckingham and Corner<sup>22</sup> have computed tables of theoretical second virial coefficients and Joule-Thomson coefficients based on such a four-constant potential function,<sup>23</sup> but they have not yet published analyses of the existing

<sup>17</sup> J. C. Slater, *Phys. Rev.*, **32**, 349 (1928).

<sup>18</sup> The unrealistic maximum at small  $r$ , and the singularity at the origin, given by Equation (74.5), are easily eliminated. The integrand of Equation (78.16) has only a small value at this false maximum, and extrapolations to a proper value at the origin introduce negligible error.

<sup>19</sup> R. A. Buckingham, *Proc. Roy. Soc. (London)*, **A168**, 264 (1938).

<sup>20</sup> J. A. Beattie, J. S. Brierley, and R. J. Barriault, to be published.

<sup>21</sup> G. Kane, *J. Chem. Phys.*, **7**, 603 (1939).

<sup>22</sup> R. A. Buckingham and J. Corner, *Proc. Roy. Soc. (London)*, **A189**, 118 (1947).

<sup>23</sup> See also W. J. C. Orr, *Proc. Camb. Phil. Soc.*, **38**, 224 (1942).

data. There is little doubt that the potential energy functions obtained with the use of their tables will be more accurate than any previously given.

The above-derived intermolecular fields must now be compared with those calculated theoretically. Calculations of the repulsive forces have been made only for helium, hydrogen, and neon (Section 73). Slater's calculation for helium is in excellent agreement <sup>24</sup> with Table X. The calculations for hydrogen and neon are more approximate, and hence do not yield such good results, although the order of magnitude is correct.

Since estimates of the dispersion energy are more readily made (Section 72), a wider comparison is possible. The constant  $C$  in the Lennard-Jones attractive field can easily be obtained from Table X by the identity

$$C = 2\epsilon r_0^6 = 4\epsilon\sigma^6 \quad (81.7)$$

but it is not legitimate to compare this figure with the theoretically calculated coefficient  $C_1$  of the dipole-dipole dispersion energy, because the higher terms in the dispersion energy are omitted from the Lennard-Jones function. Since the estimates of Margenau <sup>25</sup> indicate that the dipole-quadrupole term makes appreciable contributions and must be retained, but that further terms are negligible, a better form of the potential would be

$$u(r) = \lambda r^{-12} - C_1 r^{-6} - C_2 r^{-8} \quad (81.8)$$

In terms of the depth of the potential well and the equilibrium separation, this equation gives

$$C_1 = 2\epsilon r_0^6 \left/ \left( 1 + \frac{2C_2}{3C_1 r_0^2} \right) \right. \quad (81.9)$$

Now the second virial coefficient may be considered to yield nearly correct values of  $\epsilon$  and  $r_0$ , and these may be combined with theoretical estimates of the ratio  $C_2/C_1$  (which are generally much more trustworthy than estimates of  $C_2$  or  $C_1$  separately) to derive  $C_1$  from the above equation. The results of such calculations are displayed in Table XII. It is seen in the second column that  $C_2/C_1 r_0^2$ , which is the ratio of the dipole-quadrupole energy to the dipole-dipole energy at the potential minimum, is close to 0.15 for almost all the gases; accordingly,  $C_1$  is usually about ten per cent lower than the Lennard-Jones constant  $C$ . Several alternative theoretical values of  $C_1$  are given in Table XII for comparison. Those in column I, from the one-term dispersion formula of Equation (72.3), probably represent lower limits, while those of column II, from Kirkwood's Equation (72.5), certainly give upper limits. Column III gives values calculated by special methods; these vary somewhat in accuracy but are in general the best available estimates.

<sup>24</sup> When used in conjunction with the attractive field deduced from the virial coefficients by de Boer and Michels, Slater's repulsive energy leads to  $r_0 = 2.90 \text{ \AA}$ , while Table X gives  $2.88 \text{ \AA}$ .

<sup>25</sup> H. Margenau, *Rev. Mod. Phys.*, 11, 1 (1939).

TABLE XII  
DISPERSION FORCES FROM SECOND VIRIAL COEFFICIENTS COMPARED  
WITH THEORETICAL VALUES  
(Values of  $2\epsilon r_0^6$  and  $C_1$  in  $\text{erg-cm}^6 \times 10^{60}$ )

Gas <sup>a</sup>	$C_2/C_1 r_0^2$	$2\epsilon r_0^6$	$C_1$ (exp)	$C_1$ (theor.)		
				I <sup>b</sup>	II <sup>c</sup>	III
He.....	0.187	1.57	1.39	1.23	1.62	1.37 <sup>d</sup> , 1.39 <sup>e</sup>
Ne.....	0.156	8.37	7.5	4.7	9.6	
Ar.....	0.147	105	95	55	110	64 <sup>f</sup>
Kr.....	0.158	204	183	107	288	
Xe.....	0.147	556	500	233	732	
H <sub>2</sub> .....	0.253	12.7	10.8	11.4	12.8	10.2 <sup>g</sup> , 14.3 <sup>h</sup>
N <sub>2</sub> .....	0.125	125	115	57	106	
CH <sub>4</sub> .....	0.153	240	217	112	163	

<sup>a</sup> Values of  $C_2/C_1$  from H. Margenau, *Rev. Mod. Phys.*, 11, 1 (1939). Values of  $r_0$  and  $\epsilon$  from Table X.

<sup>b</sup> From one-term dispersion formula, Equation (72.3), as calculated by H. Margenau, *loc. cit.*

<sup>c</sup> From Kirkwood formula, Equation (72.5).

<sup>d</sup> Variational calculation with very accurate (Hylleraas) wave-function for helium. T. D. H. Baber and H. R. Hasse, *Proc. Camb. Phil. Soc.*, 33, 253 (1937).

<sup>e</sup> Two-term dispersion formula. H. Margenau, *Phys. Rev.*, 56, 1000 (1939).

<sup>f</sup> Perturbation calculation with one-electron wave-functions including exchange (Hartree-Fock). J. K. Knipp, *Phys. Rev.*, 55, 1244 (1939).

<sup>g</sup> Two-term dispersion formula. H. Margenau, *Phys. Rev.*, 63, 131 (1943).

<sup>h</sup> Variational calculation with approximate (Wang or Coulson) wave-functions for H<sub>2</sub>. H. S. W. Massey and R. A. Buckingham, *Proc. Roy. Irish Acad.*, 45, 31 (1938).

The values of  $C_1$  deduced from the virial coefficients lie between the theoretical lower and upper limits in almost every case. For helium, the agreement with the two accurate values of column III is excellent, and for hydrogen it is also very satisfactory. For argon, Knipp's figure is surely too low, since with the same wave-functions he calculated a polarizability for argon 22 per cent below the observed value. If proportionality between  $C_1$  and  $\alpha^{3/2}$  is assumed, as in Equations (72.4) and (72.5), Knipp's value of  $C_1$  may be corrected to  $92 \times 10^{-60}$   $\text{erg-cm}^6$ , in excellent agreement with the derived figure. It may be concluded that theory and experiment are generally in good accord.

Nitrogen and methane, however, deserve further attention. For these gases, the derived values of  $C_1$  are definitely too large, and agreement can be attained with a Lennard-Jones potential only by increasing the exponent  $n$  of the repulsive energy. Thus, for nitrogen Wohl <sup>26</sup> found that with  $C = 51.4 \times 10^{-60}$   $\text{erg-cm}^6$  (which is somewhat low) it was necessary to use  $n = 21.8$  to fit the observed second virial coefficients, and similar results can be obtained for

<sup>26</sup> K. Wohl, *Z. physik. Chem.*, B14, 36 (1931).

methane. The use of higher exponents than 12 for polyatomic gases is justifiable, for the repulsive energy should depend more nearly on the separation of the closest nuclei than on that of the centers of mass, and thus would more reasonably have the form  $\lambda'(r - d)^{-12}$ , where  $d$  is a constant distance. In methane, for example, we may estimate  $d$  to be about 1.6 Å, which is twice the difference between the "van der Waals radii" of CH<sub>3</sub> (2.0 Å) and H (1.2 Å) as given by Pauling.<sup>27</sup> But we wish to use the form  $\lambda r^{-n}$  to represent the repulsive energy. If the two functions are made to agree as well as possible in the range of interest (say from 3.8 to 4.3 Å for  $r$ ),  $n$  must be about 20. For bulkier molecules such as tetramethylmethane, even larger exponents would be expected.

It may finally be mentioned that rough estimates of intermolecular energies may be obtained from the constants of the Beattie-Bridgeman equation or from the critical constants. These are considered in relation to the theory of corresponding states in a later paragraph.

**(82) Second Virial Coefficients and Intermolecular Forces; Non-spherical, Non-polar Molecules:** When the molecules of a gas are not spherically symmetrical, the difficulty of obtaining reliable estimates of the intermolecular forces from the second virial coefficient is greatly increased. In the first place, the theory of the forces between asymmetric molecules has not been developed sufficiently to offer adequate guidance in the choice of a potential function; and secondly, the requirement of integrating over at least four variables, as compared to only one for the spherical case, results in much more complicated analytical expressions, even with the simplest reasonable expressions for the potential.

In the previous section, it was seen that the second virial coefficients of hydrogen and nitrogen conform well to the equations deduced for monatomic gases. In fact, rather high asymmetry is required before deviations from these equations become appreciable. For empirical purposes, it is fortunate that an asymmetric molecule may so frequently be described as equivalent to a fictitious spherical molecule, but the intermolecular potential thus derived has of course a very limited significance. It is easy to see mathematically why the spherical approximation is so often successful. Let the symbol  $\Omega$  represent the set of angular variables specifying the relative orientation of two non-spherical molecules. The intermolecular potential energy can always be put into the form

$$u(r, \Omega) = v(r) + w(r, \Omega)$$

with

$$\int_{\text{all } \Omega} w d\Omega = \langle w \rangle_{\text{av}} = 0 \quad (82.1)$$

that is,  $v(r)$  is the value of  $u$  after averaging over all orientations, at a fixed separation  $r$  of the molecular centers of mass. The second virial coefficient may

<sup>27</sup> L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, 2nd edition, 1940), p. 189.

correspondingly be written

$$B(T) = 2\pi N_0 \int_0^\infty r^2(1 - e^{-v/kT})dr + 2\pi N_0 \int_0^\infty \int_{(\Omega)} e^{-v/kT}(1 - e^{-w/kT})r^2drd\Omega \quad (82.2)$$

where  $d\Omega$  is normalized to give unity when integrated over all orientations. The first term is the result for a gas of spherical molecules obeying a potential  $v(r)$ . Since  $w$  has been defined so that its average value vanishes, the second term will be unimportant as long as  $\langle w^2 \rangle_{\text{av}}/kT$  is small compared to  $v$ , and will therefore be appreciable only for quite asymmetric fields, or at low temperatures.

Very few attempts seem to have been made to obtain explicit results for non-spherical, non-polar gases. Keesom<sup>1</sup> considered particles whose mutual repulsions were those of rigid ellipsoids, but his equations have found little application. Recently Corner<sup>2</sup> has discussed molecules of cylindrical symmetry, such as nitrogen, carbon dioxide, and ethane. The molecular model he used is that of several centers of force evenly spaced along the cylindrical axis, the potential energy between two such centers of force on different molecules being assigned the Lennard-Jones form of Equation (74.4). It was recognized that such a model could not be quantitatively correct; nevertheless, it should demonstrate at least approximately the effects of increasing asymmetry on the virial coefficient. The resultant intermolecular energy, which is the sum of the potentials between all interacting pairs of force-centers, was evaluated numerically for a large number of representative orientations, and these results were then expressed by a tractable empirical function of the angular variables, such that integration of Equation (80.2) was feasible. Examining models with two, three, and four centers of force, Corner found the latter two to give virtually identical results, and adopted the four-center model for his final treatment. The intermolecular potential thus defined is characterized by three parameters, which may be chosen in several different ways. Those used by Corner are: (1) the separation,  $r_0$ , corresponding to the minimum in the Lennard-Jones interaction between a pair of force-centers; (2) an energy parameter,  $\epsilon$ , differing slightly<sup>3</sup> from the average over all orientations of the depth of the potential trough; (3) the distance,  $2l$ , between the extreme force-centers of the molecular model, which is set equal to the extreme internuclear distance in the molecule.

Space does not permit a full account of Corner's procedure, nor of his analytical formulae for  $B(T)$ , but the results will be briefly described. Even though his integration does not conform precisely to the operations of Equations

<sup>1</sup> W. H. Keesom, *Proc. Acad. Sci. Amsterdam*, **15** (1), 240 (1912).

<sup>2</sup> J. Corner, *Proc. Roy. Soc.*, **A192**, 275 (1948).

<sup>3</sup> Actually,  $\epsilon$  is defined as the square of the average value of the square root of the depth of the potential trough, since this was convenient in carrying out the integrations. Over the range of asymmetries considered,  $\epsilon$  is always within three per cent of the average depth.

(82.1) and (82.2), Corner found that a very large part of the second virial coefficient (usually over ninety per cent until well below the critical temperature) corresponded to that of a gas of spherical molecules with a potential characterized by a depth  $\epsilon$  and by a minimum-distance  $r_0'$  somewhat greater than the value  $r_0$  corresponding to interaction between a single pair of force-centers. The constants derived <sup>4</sup> by Corner for a number of non-spherical non-polar <sup>5</sup> gases are collected in Table XIII. Methane, though essentially

TABLE XIII  
POTENTIAL ENERGY CONSTANTS FOR CYLINDRICAL NON-POLAR MOLECULES <sup>1</sup>

Gas	$\epsilon/k$	$l/r_0$	$r_0(\text{\AA})$	$r_0'(\text{\AA})$	$kT_c/\epsilon$	$V_c/10^{24}r_0^3$
N <sub>2</sub> .....	95°	0.15	3.78	4.13	1.33	1.29
CO.....	98°	0.14	4.04	4.38	1.37	1.07
CO <sub>2</sub> .....	198°	0.29	4.01	4.74	1.54	0.90
CH <sub>4</sub> .....	148°	0	4.25	4.25	1.29	1.28
C <sub>2</sub> H <sub>4</sub> .....	192°	0.21	4.6	5.2	1.47	0.92
C <sub>2</sub> H <sub>6</sub> .....	206°	0.19	5.0	5.6	1.48	0.82
Propane.....	228°	0.25	5.5	6.3	1.62	0.78
Propylene.....	220°	0.26	5.5	6.4	1.66	0.70
Trans-2-butene.....	281°	0.38	5.5	6.8	1.53	0.75
n-Butane.....	254°	0.39	5.5	6.9	1.68	0.77

<sup>1</sup> J. Corner, *Proc. Roy. Soc.*, A192, 275 (1948).

spherical, has been included to afford comparison with the other hydrocarbons. For the last four of these, the value of  $r_0$  was purposely chosen to be the same, at the expense of some accuracy in fitting the data. The last two columns show that the critical constants no longer serve to give satisfactory estimates of the intermolecular energy. The values of  $\epsilon$  and  $r_0'$  given for N<sub>2</sub> and CO are seen to be in good accord with those earlier obtained (Table X) on the assumption that these molecules were spherical.

Empirically, all the gases listed in Table XIII have virial coefficients which can be adequately represented by the Beattie-Bridgeman expression of Equation (5.6).

(83) **Second Virial Coefficients and Intermolecular Forces; Polar Molecules:** The orientation effect of Section 70 contributes an important part of the van der Waals forces between polar molecules, but Table VII shows that the dispersion effect must always be considered, as can be confirmed <sup>1,2</sup> by examination of the experimental virial coefficients for highly polar gases. The simplest potential-energy function applicable to such substances is therefore that of

<sup>4</sup> In obtaining the potential constants, the existing low-pressure Joule-Thomson coefficients, related to the second virial coefficient by Equation (3.8), were also used.

<sup>5</sup> Carbon monoxide has a sufficiently small dipole moment to be included in this group.

<sup>1</sup> H. Margenau, *Phys. Rev.*, 36, 1782 (1930).

<sup>2</sup> G. Briegleb, *Z. physik. Chem.*, B23, 105 (1933).

Equation (74.8), which contains the four constants  $\lambda$ ,  $n$ ,  $C$ , and  $\mu$ . When this function is substituted into Equation (80.2) for the second virial coefficient, the integration can be carried out analytically by methods similar to those of Keesom and Lennard-Jones for simpler cases. The result <sup>3</sup> is too lengthy to be written here in detail, but its application will presently be described. In fitting this expression to the observed second virial coefficients of steam and ammonia, which are confined to temperatures well below the Boyle temperature, it was found that almost any exponent  $n$  in the repulsive energy will give an adequate fit, including the infinite value corresponding to hard-sphere repulsion.<sup>4</sup> The value of 12 which was most convenient for the non-polar gases is also suitable here, and Hirschfelder, McClure, and Weeks <sup>5</sup> made some calculations based on this choice. Recently Rowlinson <sup>6</sup> has computed an extensive and useful table of this function and applied it to a number of polar gases. With the repulsive exponent fixed at 12, the potential energy of Equation (74.8) can be written

$$u/4\epsilon = (\sigma/r)^{12} - (\sigma/r)^6 - (\mu^2/4\epsilon\sigma^3)(\sigma/r)^3g \quad (83.1)$$

where  $g$  is the function of orientation previously given. Since the dipole moment  $\mu$  can be independently measured, the only two adjustable parameters are  $\epsilon$  and  $\sigma$ . It is to be noted that these quantities are not generally the depth of the potential-well and the zero-distance, for these now depend strongly on orientation;<sup>7</sup> only when  $\mu$  is zero, or for such special orientations that  $g$  is zero, do  $\epsilon$  and  $\sigma$  have this significance. The resulting second virial coefficient has the form

$$B/\beta = F(kT/\epsilon, t) \quad (83.2)$$

with

$$\beta = 2\pi N_0 \sigma^3/3, \quad t = \mu^2/8^{1/2}\epsilon\sigma^3$$

The function  $F$  is that tabulated by Rowlinson for round values of  $kT/\epsilon$  and  $t$ , the latter constant being chosen with the numerical factor  $8^{-1/2}$  purely for mathematical convenience. This expression reduces to the Lennard-Jones function of Equation (81.2) when  $t$  is zero. The virial coefficients of the substances listed in Table XIV are well represented by the theoretical function with the constants there given as determined by Rowlinson. It is seen that the order of increasing effective polarity, as measured by the dimensionless constant  $t$ , is far from identical with that of increasing dipole moment. The last two columns of the table give quantities of perhaps greater interest than the parameters  $\sigma$  and  $\epsilon$ . The distance  $r_0$  is the equilibrium separation of the molecules when oriented for maximum dipole attraction (head-to-tail,  $g = 2$ ),

<sup>3</sup> W. H. Stockmayer, *J. Chem. Phys.*, 9, 398 (1941).

<sup>4</sup> It was pointed out with reference to Equations (81.1) and (81.2) that a similar situation holds for non-polar gases unless the measurements extend to well above the Boyle temperature.

<sup>5</sup> J. O. Hirschfelder, F. T. McClure, and I. F. Weeks, *J. Chem. Phys.*, 10, 201 (1942).

<sup>6</sup> J. S. Rowlinson, *Trans. Faraday Soc.*, 45, 974 (1949).

<sup>7</sup> For some orientations, there may be no minimum, for dipole repulsion may overshadow the dispersion effect.



and  $\Delta U$  is the interaction energy,  $2\mu^2/r_0^3$ , between the permanent dipoles when in this orientation, being therefore less by  $\epsilon$  than the dissociation energy of the pair of molecules in their most stable configuration.

Several interesting features emerge from the figures of Table XIV. In the first place, it should be pointed out that the temperature range of experiment was so short for chloroform, acetone, methanol, and acetonitrile that the con-

TABLE XIV  
POTENTIAL ENERGY CONSTANTS FOR POLAR GASES<sup>a</sup>

Substance	$\mu \times 10^{18}$ e.s.u.	$t$	$\sigma(\text{\AA})$	$\epsilon$ (cal/mole)	$r_2(\text{\AA})$	$\Delta U$ (cal/mole)
$\text{CHCl}_3$ .....	1.05	0.1	2.99	2,110	3.30	860
$\text{CH}_2\text{Cl}_2$ .....	1.89	0.6	3.44	750	3.60	2,020
$\text{CH}_3\text{COCH}_3$ .....	2.74	0.7	3.76	1,030	3.91	3,280
$\text{CH}_3\text{OH}$ .....	1.66	0.8	2.40	1,260	2.49	4,660
$\text{NH}_3$ .....	1.47	1.0	2.58	630	2.66	2,960
$\text{H}_2\text{O}$ .....	1.83	1.2	2.65	760	2.68	4,440
$\text{CH}_3\text{CN}$ .....	3.5	1.2	4.02	800	4.07	4,640
$\text{CH}_3\text{CHO}$ .....	2.7	1.4	3.68	530	3.68	3,680

<sup>a</sup> J. S. Rowlinson, *Trans. Faraday Soc.*, 45, 974 (1949).

stants can scarcely be regarded as unique in these cases. For the other substances, they may be taken more seriously. The results for steam appear highly satisfactory. Thus, the distance  $r_0$  is agreeably close to the O—O distance of 2.76 Å persisting in ice, and the maximum dipole attraction energy  $\Delta U$  is in excellent agreement with the hydrogen-bond energy of 4.5 kcal estimated by Pauling<sup>8</sup> from the heat of sublimation of ice. Furthermore, the coefficient,  $C = 4\epsilon\sigma^6$ , of  $r^{-6}$  in the potential energy is found to be  $72 \times 10^{-60}$  erg-cm<sup>6</sup>, which corresponds (after subtraction of the induction effect and of the dipole-quadrupole induction term) to a value of  $49 \times 10^{-59}$  erg-cm<sup>6</sup> for the coefficient  $C_1$  of the dipole-dipole dispersion energy, in excellent agreement with that estimated by London (Table VII). Similarly good results are obtained with other choices ( $n = 24$  or infinite) for the repulsive index.<sup>9</sup>

For ammonia, Table XIV gives somewhat too small a dispersion energy, and too small a value of  $\sigma$  as compared to the N—N distance of 3.38 Å in the solid. The value of  $\Delta U$  is also rather high compared to Pauling's estimate of 1.3 kcal for the strength of the N—H—N bond. The distances also seem too small for some of the other gases; certainly  $\sigma$  should be no smaller for chloroform and methyl chloride than for methane (Table X). A part of the difficulty is probably due to the fact that the potential energy of Equation (83.1) corresponds to a dipole located at the center of mass of the molecule; this is obviously not true for methanol, which also appears to have too small a value of  $\sigma$ .

<sup>8</sup> L. Pauling, *Nature of the Chemical Bond* (Cornell University Press, 1940), Chap. X.

<sup>9</sup> Stockmayer, *loc. cit.*

Another valid and fundamental criticism of these results is found in the work of Margenau and Myers,<sup>10</sup> who investigated the permanent charge distribution of the water molecule and showed that the interactions involving the permanent quadrupoles may not be neglected. Including these additional terms in the orientation effect, and using a slightly lower estimate of the dispersion forces, they were able to fit the virial coefficients of steam by adjustment of the repulsive energy. It thus appears that the potential of Equation (83.1) is not sufficiently general<sup>11</sup> to describe in detail the interactions between all polar molecules; but it permits an excellent fit of the data with only two disposable constants ( $\epsilon$  and  $\sigma$ ) and certainly gives molecular parameters of at least the correct order of magnitude.

An alternative treatment of highly polar gases is described in the following section.

(84) **Chemical Association:** Formally, the imperfections of a gas can be attributed to the formation of double, triple, and larger molecules, as governed by the law of mass action for perfect gases. Consider the simple case in which  $n$  formula-weights of a gas are distributed into  $n_1$  moles of monomer and  $n_2$  moles of dimer, governed by the equilibrium law

$$n_2 = K_c n_1^2 / V \quad (84.1)$$

and the conservation law,  $n = n_1 + 2n_2$ . Assuming the gas mixture to be perfect and the dimerization to be small, we find

$$pV/nRT = 1 - K_c(n/V) + \dots \quad (84.2)$$

to terms of order  $(n/V)$ . Thus the second virial coefficient  $B(T)$  appears as the negative of the association-constant  $K_c$ . However, to be consistent to terms in  $(n/V)$  we should recognize the "excluded volume"  $b$  offered by the dimers toward the remaining monomers, and thus put

$$B(T) = b - K_c \quad (84.3)$$

If some objective and physically justifiable procedure for determining  $b$  can be set up, the dimerization constant can be evaluated from the second virial coefficient and its temperature-dependence used to determine energies and entropies of formation in the conventional manner.

In Section 79 it was shown that the quantum theory of the second virial coefficient gives added formal justification to such a procedure. There it was shown that  $B(T)$  is composed of two parts, one of which ( $B_{\text{cont.}}$ ) plays the role of  $b$  as used above, and the other of which ( $B_{\text{discr.}}$ ) is the negative of the dimerization constant. A related argument<sup>1</sup> can be based on the classical Equation (78.16) as follows, spherical molecules being considered for conveni-

<sup>10</sup> H. Margenau and V. W. Myers, *Phys. Rev.*, **66**, 307 (1944).

<sup>11</sup> It is easy to see that Equation (83.1) is incapable, for example, of predicting the correct crystal structure of ice, where each water molecule is hydrogen-bonded to four neighbors.

<sup>1</sup> J. O. Hirschfelder, F. T. McClure, and I. F. Weeks, *J. Chem. Phys.*, **10**, 201 (1942).

ence. Let a dimer be arbitrarily defined as any pair of monomers lying within some distance  $r^*$  of each other, and choose  $r^*$  large enough (say several molecular "diameters") so that the integrand of Equation (78.16) is negligible for all larger distances; loosely,  $r^*$  is the "range" of the intermolecular forces. Equation (78.16) can then be split in the following way:

$$B(T) = 2\pi N_0 \int_0^{r^*} r^2 dr - 2\pi N_0 \int_0^{r^*} r^2 e^{-u/kT} dr + 2\pi N_0 \int_{r^*}^{\infty} r^2 (1 - e^{-u/kT}) dr \quad (84.4)$$

The first term of the right-hand member is seen to be an "excluded volume," which can thus be identified with  $b$ ; and the second term corresponds to the classical formula for an association constant. The third term will be negligible if  $r^*$  is properly chosen and the forces are of the usual type.<sup>2</sup>

Although this quasi-chemical approach can always be used, it is obviously unattractive unless  $B(T)$  has a large negative value; in this case the choice of  $b$ , though still arbitrary, can have little effect on the derived value of  $K_c$ . In practice, the concept of association is generally adopted for one or more of the following reasons:

(a) The second virial coefficient has a value considerably more negative than that predicted by the law of corresponding states, with the non-polar spherical molecules as a norm.

(b) The molecular structure allows the formulation of a definite dimer, involving a hydrogen bond or covalent bond.

(c) Dimeric species have been detected spectroscopically, or by other independent physical means.

Thus, for example, the vapors of formic and acetic acids (hydrogen bonding) and of nitrogen dioxide (covalent bonding) are always considered to be mixtures of monomer and dimer; gaseous methanol and steam (weaker hydrogen bonding) are often so considered; and the gaseous normal paraffins are rarely considered to be associated.

If the quasi-chemical treatment is adopted, Equation (84.3) can be rewritten in the form

$$B(T) = b - e^{\Delta S^0/R} e^{-\Delta E^0/RT} \quad (84.5)$$

in which  $\Delta S^0$  and  $\Delta E^0$  are the standard <sup>3</sup> entropy and energy of dimerization.

<sup>2</sup> Scatchard (private communication) has pointed out that the approximate radial distribution-function  $r^2 e^{-u/kT}$ , calculated with the Lennard-Jones potential of Equation (74.4), displays a minimum, at values of  $r$  between  $r_0$  and  $2r_0$ , when  $kT/\epsilon$  is less than  $\frac{3}{2}$ , which is slightly above the critical temperature. For sufficiently low temperatures, therefore,  $r^*$  could be chosen in this way without ambiguity. This would be completely analogous to Bjerrum's treatment of ion association in concentrated solutions of electrolytes.

<sup>3</sup> With the definition of  $K_c$  given in Equation (84.1), the standard state is the hypothetical perfect gas at a concentration of one mole per unit volume.

Thus, even in the simplest case there are three adjustable parameters ( $b$ ,  $\Delta S^\circ$ ,  $\Delta E^\circ$ ), so it is not surprising that a good fit of the experimental results can be obtained with such an expression; indeed, the data usually are insufficiently numerous or exact to determine a unique set of constants. Hirschfelder, McClure, and Weeks have shown that the arbitrary choice  $b = 1.75v_c$  generally works well, and have in this way estimated dimerization constants for a number of polar and non-polar gases.

Lambert, Roberts, Rowlinson, and Wilkinson,<sup>4</sup> in discussing their measurements on the virial coefficients of certain organic vapors, used another method, which has been further discussed by Rowlinson.<sup>5</sup> This consists of taking the quantity  $b$  not as a constant, but as equal to the second virial coefficient predicted from the critical constants of the substance by means of the reduced equation of Berthelot (Table I). The dimerization energy found from the temperature-dependence of  $K_c$  is then considered to be due entirely to electrostatic forces (dipole and multipole attractions, hydrogen bonding). This procedure can be justified if the intermolecular potential energy  $u$  is made up of two parts,  $v$  and  $w$ , of which the latter is negligible at most intermolecular separations and orientations but becomes dominant (large and negative) in a restricted small range  $\delta$  of the configurational variables. Defining  $d\Omega$  as the differential of all the orientation variables, normalized so that its integral over all values is unity, we may then write the second virial coefficient approximately as

$$B(T)/2\pi N_0 \cong \int_0^\infty \int_{(\text{all } \Omega)} (1 - e^{-v/kT}) r^2 dr d\Omega - \int \int_{(\delta)} e^{-w/kT} r^2 dr d\Omega \quad (84.6)$$

The first term would then correspond to the virial coefficient to be expected if the specific forces causing dimerization were absent, and the second is an equilibrium constant in which only the energy  $w$  is involved. Empirical evidence for the validity of this method is furnished by the fact that the energies of dimerization found for acetonitrile, methyl chloride, acetaldehyde, steam, and ammonia are in remarkably good agreement with the dipole energies  $\Delta U$  calculated by the method of Section 83.

#### GASES AT HIGHER PRESSURES

**(85) Theory of Corresponding States:** In the early sections of this chapter, the principle of corresponding states was discussed in relation to graphical methods of correlation and to several empirical equations of state. Here the theoretical basis of the principle is briefly considered.

It is easy to show that a group of pure substances will obey the law of corresponding states exactly if the following two assumptions are valid:

<sup>4</sup> J. D. Lambert, G. A. H. Roberts, J. S. Rowlinson, and V. J. Wilkinson, *Proc. Roy. Soc. (London)*, **A196**, 113 (1949).

<sup>5</sup> J. S. Rowlinson, *Trans. Faraday Soc.*, **45**, 974 (1949).

(a) The systems all obey the laws of classical statistical mechanics.

(b) The intermolecular potential energy has the same analytical form for each substance, and is characterized by just two independent constants for each substance.

Let us choose these two constants to be a characteristic energy  $\epsilon$  and a characteristic distance  $\sigma$ , as for example in the case of the Lennard-Jones potential. Then there is a functional relation<sup>1</sup>

$$f(p, kT, V/N, \epsilon, \sigma) = 0 \quad (85.1)$$

where assumption (a) allows us to omit the molecular mass, and assumption (b) assures us that the function  $f$  has the same form for all the gases. A very simple dimensional analysis<sup>2</sup> then suffices to show that between the dimensionless variables

$$\begin{cases} p^* = p\sigma^3/\epsilon \\ v^* = V/N\sigma^3 \\ T^* = kT/\epsilon \end{cases} \quad (85.2)$$

there must exist a functional relation,

$$f(p^*, v^*, T^*) = 0 \quad (85.3)$$

which is the same<sup>3</sup> for all the substances. The same conclusion can be reached by a more lengthy procedure making direct appeal to the configuration integral.<sup>4</sup>

The conditions  $(\partial p^*/\partial v^*)_{T^*} = 0$  and  $(\partial^2 p^*/\partial v^{*2})_{T^*} = 0$ , together with Equation (85.3) itself, must lead to unique numerical values of the dimensionless variables  $p^*$ ,  $v^*$ ,  $T^*$  at the critical point. Thus Equation (85.3) is easily transformed by a simple change of scale into the more customary statement of the corresponding-states principle in terms of the reduced variables  $p/p_c$ ,  $v/v_c$ , and  $T/T_c$ .

In Table XV, values of  $p_c^*$ ,  $v_c^*$ , and  $T_c^*$  are listed for a few gases, the potential constants  $\sigma$  and  $\epsilon$  being taken from Table X (Section 81) and the critical data from various sources. It is seen that with the notable exception of helium and hydrogen, and perhaps of neon, the values are nearly the same. Thus the Lennard-Jones constants may be roughly determined, for heavy spherical molecules, from the equations

$$kT_c/\epsilon \cong 1.28 \quad (85.4)$$

and

$$V_c/N\sigma^3 \cong 3.10 \quad \text{or} \quad p_c\sigma^3/\epsilon \cong 0.120$$

In Section 7 it was shown that the principle of corresponding states can be used to construct a reduced form of the Beattie-Bridgeman equation of state,

<sup>1</sup> The volume per molecule,  $V/N$ , has been used because  $p$  must be an intensive property.

<sup>2</sup> See, for example, A. W. Porter, *The Method of Dimensions* (Methuen, London, 1933).

<sup>3</sup> The function in Equation (85.3) is of course not identical with that of (85.1).

<sup>4</sup> See, for example, J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (Wiley, 1940) pp. 269-272.

or indeed of any semi-empirical equation. The five Beattie-Bridgeman constants were all expressed in terms of two characteristic constants of the gas,  $p_c$  and  $T_c$ . They could therefore equally well be expressed in terms of the two potential-energy constants  $\epsilon$  and  $\sigma$ . This was done by Hirschfelder and Roseveare,<sup>5</sup> who deduced the relations

$$2\pi N_0 \sigma^3 / 3 = 1.25 B_0; \quad \epsilon / k = 0.300 A_0 / R B_0 \quad (85.5)$$

from a comparison of the expressions (5.6) and (81.2) for the second virial coefficient. These formulae are most successful for the heavier spherical molecules, as would be expected.

TABLE XV  
CRITICAL CONSTANTS AND POTENTIAL-ENERGY CONSTANTS

Substance	$kT_c/\epsilon$	$V_c/N\sigma^3$	$p_c\sigma^3/\epsilon$	$NkT_c/p_cV_c$
He.....	0.51	5.74	0.0274	3.26
Ne.....	1.24	3.39	0.109	3.36
Ar.....	1.27	3.16	0.118	3.42
Kr.....	1.22	3.28	0.107	3.45
Xe.....	1.29	3.00	0.127	3.42
H <sub>2</sub> .....	0.90	4.35	0.0635	3.26
N <sub>2</sub> .....	1.32	3.08	0.125	3.42
CH <sub>4</sub> .....	1.29	3.04	0.123	3.46

The failure of the lightest gases to conform to Equations (85.4) must be due to quantum effects, as should already be clear from the discussion of Sections 79 and 81. The molecular mass and the Planck constant must therefore be introduced into the functional relationship of Equation (85.1); but from the Schrödinger equation it follows that they must appear always in the ratio  $\hbar^2/m$ . Dimensional analysis then gives a modified corresponding-states law,

$$f(p^*, v^*, T^*, \Lambda^*) = 0$$

with

$$\Lambda^* = \hbar / (m\epsilon\sigma^2)^{1/2} \quad (85.6)$$

which must of course reduce to the relationship of Equation (85.3) in the limit that  $\Lambda^*$  vanishes. The dimensionless constant  $\Lambda^*$  will be recognized as one already prominent in the discussion of quantum effects in Sections 79 and 81, the order of increasing deviations from classical corresponding states being that of increasing  $\Lambda^*$ . With Equation (85.6), it no longer follows that  $p^*$ ,  $v^*$ , and  $T^*$  have unique values at the critical point, for they will depend on  $\Lambda^*$ . A striking demonstration of the validity and utility of Equation (85.6), which might well be called the quantum-theoretical principle of corresponding states,

<sup>5</sup> J. O. Hirschfelder and W. E. Roseveare, *J. Phys. Chem.*, **43**, 15 (1939).

is the successful prediction by de Boer <sup>6</sup> of the vapor pressures and critical constants of the light helium isotope He<sup>3</sup>.

Failure of the classical principle of corresponding states is not limited to the very light gases, but occurs also for highly asymmetric or polar molecules, whose intermolecular potentials require more than two constants for their description. If only three constants were required, as for the models discussed in Sections 82 and 83, useful modifications of the classical corresponding-states law, similar to that of Equation (85.6), could be formulated. For polar gases conforming to the potential of Eq. (83.1), for example, we would have

$$f(p^*, v^*, T^*, \mu^2/\sigma^3\epsilon) = 0$$

which could also be written

$$f(p/p_c, v/v_c, T/T_c, \mu^2/v_c T_c) = 0 \quad (85.7)$$

The fourth variable for the case of asymmetric non-polar molecules would be the ratio  $l/r_0$  (see Section 82) defining their shape. While modified corresponding-states laws of this type have been pointed out,<sup>7</sup> they do not seem to have been much developed for practical purposes, though this would seem highly desirable.

Finally, we may remark that when  $\Lambda^*$  is small the quantum correction to the second virial coefficient can be conveniently written in terms of the critical constants. Corner <sup>8</sup> gives the equation

$$B^{(1)} = \frac{45v_c^{1/3}}{MT} \left( 1 + 11 \frac{T_c}{T} \right) \quad (85.8)$$

with  $B^{(1)}$  and  $v_c$  in cm<sup>3</sup>/mole,  $M$  in grams/mole, and  $T$  in Kelvin degrees. This was already given in another form as Equation (81.5).

(86) **Statistical Theory of the Complete Equation of State:** In this section is presented a necessarily abbreviated account of the general imperfect gas theory developed by Ursell, Mayer, and others.<sup>1</sup> For simplicity, we treat a pure, classical, monatomic gas with complete additivity of forces, though each of these restrictions can be shown not to invalidate the general form of the result.<sup>2</sup> The starting-point is the configuration integral

$$Q_\tau = \int \cdots \int e^{-U/kT} d\tau_1 \cdots d\tau_N \quad (86.1)$$

already considered in Section 78, to which the development here followed should

<sup>6</sup> J. de Boer, *Physica*, **14**, 139 (1948); J. de Boer and R. Lunbeck, *Physica*, **14**, 510 (1948).

<sup>7</sup> J. O. Hirschfelder, F. T. McClure, and I. F. Weeks, *J. Chem. Phys.*, **10**, 201 (1942).

<sup>8</sup> J. Corner, *Proc. Roy. Soc. (London)*, **A192**, 275 (1948).

<sup>1</sup> For a more detailed presentation, see J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (John Wiley, 1940), Chaps. 12-14.

<sup>2</sup> B. Kahn and G. E. Uhlenbeck, *Physica*, **5**, 399 (1938).

be compared. With the assumption that  $U$  is pair-wise additive, and with definition of the function

$$f_{ij} = e^{-u_{ij}/kT} - 1 \quad (86.2)$$

the integrand of Equation (86.1) can be written as

$$e^{-U/kT} = \prod_{\text{all pairs}} (1 + f_{ij}) = 1 + \sum f_{ij} + \sum \sum f_{ij}f_{kl} + \cdots \quad (86.3)$$

The analysis and classification of the terms in this sum is necessary to further progress, and is based on the physical realization that  $f_{ij}$  differs appreciably from zero only when the molecules  $i$  and  $j$  are fairly close to each other (Fig. 7). Any term in the sum of Equation (86.3) will then contribute significantly to the integrand only when all the pairs of molecules designated by the  $f$ 's appearing in it are actually close together. As an example of such a term, consider the product  $f_{12}f_{57}f_{58}f_{78}f_{69}$ . This term will have an appreciable value only for such configurations of the entire gas that the indicated pairs of molecules lie close together, all the other molecules of the gas lying well apart from each other. Following Mayer, it is convenient to say that any such term corresponds to the distribution of the gas molecules into *clusters* of interacting molecules. The example given corresponds to a configuration of the gas in which there are two binary clusters (molecules 1-2 and 6-9), one ternary cluster (molecules 5-7-8), and all the other ( $N - 7$ ) molecules are separate ("single" clusters). In general, such a term designates the partition of the molecules into  $m_1$  single clusters,  $m_2$  binary clusters,  $\cdots$ ,  $m_l$  clusters of  $l$  molecules,  $\cdots$ , governed by the conservation law

$$N = \sum_l l m_l \quad (86.4)$$

We next note that there will usually be more than one term corresponding to the same assignment of molecules to clusters. Thus the terms  $f_{12}f_{69}f_{57}f_{58}$ ,  $f_{12}f_{69}f_{57}f_{78}$ , and  $f_{12}f_{69}f_{58}f_{78}$  all lead to the same clusters as the example previously considered, since molecules 5, 7, and 8 form a ternary cluster even if only two of the three possible pair-wise interactions are appreciable. In general, it can be seen that any factor which defines a cluster of  $l$  molecules must consist of a product of at least  $(l - 1)$   $f$ -functions (since at least  $l - 1$  links are required to connect  $l$  objects together) and at most  $l(l - 1)/2$   $f$ 's (in which case all possible pair-wise interactions would be appreciable). The sum of all such factors leading to a cluster of a specified size forms the integrand of a *cluster integral*  $b_l$ , defined by the equation

$$b_l = \frac{1}{l!V} \int \cdots \int \sum (\prod f_{ij}) d\tau_1 \cdots d\tau_l \quad (86.5)$$

(sum over all products consistent with a single cluster of size  $l$ ).



As examples, we give the first three such integrals:

$$b_1 = \frac{1}{V} \int d\tau_1 = 1$$

$$b_2 = \frac{1}{2V} \iint f_{12} d\tau_1 d\tau_2 = \frac{1}{2} \int_0^\infty f(r) \cdot 4\pi r^2 dr$$

$$b_3 = \frac{1}{6V} \iiint (f_{12}f_{13} + f_{13}f_{23} + f_{12}f_{23} + f_{12}f_{23}f_{13}) d\tau_1 d\tau_2 d\tau_3$$

The factor  $(l!)^{-1}$  in the definition of  $b_l$  is for later convenience. The factor  $V^{-1}$ , as can be seen explicitly for  $b_1$  and  $b_2$  above, makes  $b_l$  independent of the volume of the gas<sup>3</sup> and a function of temperature only, for after the integrations with respect to the coordinates of  $l - 1$  molecules have been completed, the final integration always gives the factor  $V$ ; compare Section 78. It is also clear that the particular numerical identifications of the molecules chosen for the cluster are immaterial, since in a pure gas all interactions are alike. Finally, it should be noticed that  $b_2$  is just half the  $\beta$  of Section 78, and is therefore closely related to the second virial coefficient.

A cluster integral gives only one factor of the contribution of any one term of Equation (86.3) to the configuration integral; the whole contribution requires integration over the coordinates of all the  $N$  molecules, and hence gives a *product* of cluster integrals. For example, the four terms previously quoted as examples, when added together, produce a contribution  $[(1!)Vb_1]^{N-7}[(2!)Vb_2]^2[(3!)Vb_3]^1$  to  $Q_\tau$ , and in general a term will give an additive contribution

$$\prod_i [(l!)Vb_l]^{m_l}$$

In order to find the total value of  $Q_\tau$ , we must now add together all such contributions, and we soon recognize that many of them will have the same value. Thus, for example, the term  $f_{24}f_{56}f_{79}f_{89}$  gives, after integration, the same contribution as  $f_{12}f_{69}f_{57}f_{78}$ , for each corresponds to two binaries and one ternary cluster. By a well-known combinatory law, there are

$$\frac{N!}{m_1!m_2!m_3!\cdots (1!)^{m_1}(2!)^{m_2}(3!)^{m_3}\cdots} = \prod_i \frac{N!}{(l!)^{m_l}m_l!}$$

ways in which the  $N$  molecules (regarded as distinguishable, as always in classical statistics) can be divided into  $m_1$  single molecules,  $m_2$  binary clusters,  $m_3$  ternary clusters, and so on. The summed contribution of all the terms corresponding to any one given set of the numbers  $m_1, m_2, m_3, \dots, m_l, \dots$  is

<sup>3</sup> This is no longer true in the liquid phase.

therefore

$$\frac{N!}{\prod_i (l!)^{m_l} m_l!} \cdot \prod_i [(l!) V b_l]^{m_l} = N! \prod_i \frac{(V b_l)^{m_l}}{m_l!}$$

To find  $Q_r$ , we must finally add up the contributions arising from *all possible* divisions of the molecules into clusters, from the one extreme that all clusters are single to the other extreme that the entire gas forms one giant cluster. We therefore finally obtain

$$\frac{Q_r}{N!} = \sum \prod_i (V b_l)^{m_l} / m_l! \quad (86.6)$$

(sum over all sets of the  $m_l$  such that  $\sum l m_l = N$ ).

The configuration integral has thus been expressed as a definite function of volume and temperature, and Equation (78.6) can be used to obtain the equation of state. However, Equation (86.6) as it stands is scarcely convenient for this purpose, and further developments are needed. The reduction of this equation can be accomplished in several ways, of which the simplest mathematically and physically is not rigorous unless all the cluster integrals are positive, which will not be true except at very low temperatures. This consists of replacing the sum of Equation (86.6) by its single largest term, corresponding to that set of the numbers  $m$  which describes the *most probable* distribution of the  $N$  molecules into clusters. This is entirely analogous to a problem arising in the statistical mechanics of perfect gases, where the most probable distribution of the molecules among the available energy levels is calculated,<sup>4</sup> and as in that case is sufficient to give the *logarithm* of  $Q_r$  though not its absolute value. Actually, there are many distributions of comparable probability, but the logarithm of their number is of the order of  $N^{1/2}$ , while the logarithm of  $Q_r$  (being an extensive property) must be proportional to  $N$ . On using the Stirling approximation for the logarithm of  $(m_l!)$ , and introducing the conservation law of Equation (86.4) by the Lagrange method of undetermined multipliers, as in the perfect-gas problem, the largest term in  $Q_r$  is found to correspond to the relation

$$m_l = V b_l Z^l \quad (86.7)$$

for the most probable number of  $l$ -sized clusters, where the multiplier  $Z$  is specified by the conservation law

$$N = \sum l m_l = V \sum l b_l Z^l \quad (86.8)$$

This last equation shows that  $Z$  is an intensive property of the gas, being a function of temperature (through the  $b_l$ ) and of the volume per molecule  $V/N$ . It will later be shown to have a familiar physical significance.

<sup>4</sup> Compare J. G. Aston, Vol. I, Chap. 4, Section 10. More rigorous treatments in each case show that these "most probable" distribution-numbers are really *average* values.

Returning to Equation (86.6), taking logarithms, and making use of Stirling's formula and of Equation (86.7), we obtain

$$\ln(Q_r/N!) = V \Sigma b_i Z^i - N \ln Z \quad (86.9)$$

The pressure, from Equation (78.6), is then given by

$$\begin{aligned} p/kT &= (\partial \ln Q_r / \partial V)_{N,T} \\ &= \Sigma b_i Z^i + \left( V \Sigma i b_i Z^{i-1} - \frac{N}{Z} \right) \frac{\partial Z}{\partial V} \\ &= \Sigma b_i Z^i \end{aligned} \quad (86.10)$$

If this result is accepted, the equation of state is given by Equations (86.8) and (86.10) involving the parameter  $Z$ . If the latter could be eliminated between these two equations, an equation of state of the usual form would be obtained. Before regarding this task, we remark that the above results can also be obtained rigorously, either by the use of a method of steepest descents,<sup>5</sup> as in the Darwin-Fowler version of statistical mechanics, or by the method of the Gibbs grand canonical ensemble.<sup>6</sup>

It is instructive to combine Equations (86.7) and (86.10) into the result

$$pV/kT = \Sigma m_i \quad (86.11)$$

which shows that each "cluster" of the most probable distribution behaves like a perfect-gas molecule with respect to its effect on the pressure. But now a difficulty arises: how can  $pV/NkT$  exceed unity (as it is observed to do over wide ranges of temperature and pressure)? This is mathematically possible only if some of the numbers  $m_i$  are negative, which seems inconsistent with their apparent physical meaning as numbers of clusters, and certainly with the mathematical procedure of using the Stirling formula for the logarithm of  $(m_i!)$ . The answer is that these numbers really represent the average numbers of clusters *in excess* of what they would be if there were no intermolecular forces, for even randomly distributed particles without interactions will fall into configurations resembling clusters. That the numbers  $m_i$  give only the excess values will appear reasonable on returning to Equation (86.2) and recognizing that the function  $f_{ij}$  gives the difference between the probability of a certain pair-wise configuration and its random value of unity.

To find the physical significance of  $Z$ , we evaluate the work-content  $A$  of the gas, using Equations (78.1), (78.5), and (86.9), and obtaining

$$\begin{aligned} A &= -kT \ln Q \\ &= \frac{3}{2} NkT \ln(h^2/2\pi mkT) - V kT \Sigma b_i Z^i + NkT \ln Z \end{aligned} \quad (86.12)$$

<sup>5</sup> M. Born and K. Fuchs, *Proc. Roy. Soc. (London)*, **A166**, 391 (1938); B. Kahn and G. E. Uhlenbeck, *loc. cit.*

<sup>6</sup> H. Snyder, *Phys. Rev.*, **62**, 63 (1942); G. S. Rushbrooke, *Introduction to Statistical Mechanics* (Oxford, 1949), Chap. XVII.

But use of Equation (86.10) for the remaining sum shows the second term on the right to be simply  $-pV$ , so that we find the Gibbs free energy,

$$F = \frac{3}{2}NkT \ln(h^2/2\pi mkT) + NkT \ln Z \quad (86.13)$$

This immediately establishes  $Z$  as the *fugacity* or *activity* of the gas, though not on the conventional scale, as  $Z$  has the dimensions of molecules per unit volume.

The elimination of  $Z$  between Equations (86.8) and (86.10) involves lengthy algebra and a difficult combinatorial problem, and will not be demonstrated here. Briefly, the cluster integrals  $b_i$  can be analyzed into sums of products of simpler, "irreducible" integrals  $\beta_k$ . These are defined as

$$\beta_k = \frac{1}{k!V} \int \cdots \int \sum (\prod f_{ij}) d\tau_1 \cdots d\tau_{k+1} \quad (86.14)$$

(sum over all products involving  $k+1$  molecules in which each molecule is connected to every other by at least two independent non-crossing paths).

The equation of state is then shown to be

$$pV/NkT = 1 - \sum_{k=1}^{\infty} \frac{k\beta_k}{k+1} \left(\frac{N}{V}\right)^k \quad (86.15)$$

so that the irreducible integrals are intimately related to the virial coefficients. In particular, it is seen that the second virial coefficient is  $-\beta_1/2$  per molecule, in agreement with Equation (78.16). Integration of Equation (86.14) to obtain the specific dependence on temperature, however, remains hopelessly complex except for the lowest several integrals. The few results to date are considered in the next section.

The development of Equation (86.15) converges in the gas region, but breaks down when the two-phase region is encountered. The most striking results of the Mayer theory concern condensation and the critical state, but these are considered in the chapter on Liquids.<sup>7</sup>

(87) **The Third and Higher Virial Coefficients:** Because of mathematical complexity, the third and fourth virial coefficients  $C$  and  $D$  of the equation

$$pV/nRT = 1 + (n/V)B + (\tilde{n}/V)^2C + (n/V)^3D + \cdots \quad (87.1)$$

have been evaluated analytically only for a gas of hard non-attracting spheres. This was accomplished long ago by Boltzmann and others,<sup>1</sup> the results being

$$\begin{aligned} B &= b = 2\pi N_0 \sigma^3/3 \\ C &= 5b^2/8 \\ D &= 0.2869b^3 \end{aligned} \quad (87.2)$$

where  $\sigma$  is the diameter.

<sup>7</sup> G. E. Kimball, this volume, Chap. III.

<sup>1</sup> See H. Happel, *Ann. Phys.*, 30, 246 (1906).

The only really useful calculations are those by de Boer and Michels<sup>2</sup> and by Montroll and Mayer<sup>3</sup> of the third virial coefficient for gases obeying the special Lennard-Jones potential of Equation (74.3). From corresponding states (Section 85) it is clear that the result must have the form

$$C(T) = \beta^2 f(kT/\epsilon); \quad \beta = 2\pi N_0 \sigma^3 / 3 \quad (87.3)$$

where  $\sigma$  and  $\epsilon$  are the potential energy constants. The integrations were performed numerically, and the graphical results presented by the two pairs of investigators do not agree completely. The experimental results for xenon<sup>4</sup> tend to support the de Boer-Michels values, which can be fitted by the equation

$$C/\beta^2 = 0.268 + 0.086(\epsilon/kT) + 0.488(\epsilon/kT)^2 \quad (87.4)$$

Both calculations, however, indicate rough proportionality between  $C$  and  $\epsilon/kT$  in the range between the Boyle and critical temperatures, and this fact may be used for interpolations or short extrapolations of experimental results.

Mayer and Ackermann<sup>5</sup> have made some very rough estimates of fourth virial coefficients, but these scarcely have quantitative utility. It is clear that further calculations are needed, and with modern facilities for computation some progress can be expected.<sup>6</sup>

## GAS MIXTURES

**(88) Forces Between Unlike Molecules:** As already pointed out in Section 9, the statistical-mechanical treatment of gas mixtures can be carried out by extension of the method described for pure gases in Section 86. It is found that the  $n$ th virial coefficient, per mole, of a mixture can be expressed as a polynomial of  $n$ th order in the mole fractions, and each coefficient is defined as an integral in configuration-space. Thus, for example, the coefficient of the term  $x_1 x_2^2 x_3^2$  in the sixth virial coefficient of a ternary gas mixture would be proportional to the "irreducible integral"  $\beta_5$  for a cluster composed of one

<sup>2</sup> J. de Boer and A. Michels, *Physica*, **6**, 97 (1939).

<sup>3</sup> E. Montroll and J. E. Mayer, *J. Chem. Phys.*, **9**, 626 (1941).

<sup>4</sup> J. A. Beattie and R. J. Barriault, unpublished results.

<sup>5</sup> J. E. Mayer and P. G. Ackermann, *J. Chem. Phys.*, **5**, 74 (1937).

<sup>6</sup> *Note added in proof:* A very accurate numerical integration of the classical third virial coefficient for the Lennard-Jones potential has recently been completed,<sup>1</sup> supplanting the earlier evaluations mentioned in Sections 3 and 87. The empirical Equation (87.4) represents the accurate theoretical function fairly well over the range of  $kT/\epsilon$  from 1.5 to 5, or from slightly above the critical temperature to well above the Boyle temperature, but it is quite inaccurate outside this range. When the theoretical third virial coefficients are compared with the available experimental results, fairly good agreement is found for argon, methane, and nitrogen. The agreement is poor for carbon dioxide, ethylene and ethane (probably because of their cylindrical molecular shape) and for hydrogen, deuterium and helium (probably because of quantum effects).

<sup>1</sup> R. B. Bird, E. L. Spotz, and J. O. Hirschfelder, *J. Chem. Phys.*, **18**, 1395 (1950). See also T. Kihara, *J. Phys. Soc. Japan*, **3**, 265 (1948).

molecule of the first species, three of the second, and two of the third. On the assumption that the forces are additive, the theory is then formally complete if the interaction between a pair of dissimilar molecules can be specified. The most convenient results could be obtained if the potential energy between such a pair were expressible by the same function describing interactions between pairs of similar molecules. If, for example, the Lennard-Jones form of Equation (74.3) could be used, the quantities  $B_{ij}$  occurring in the equation

$$B(T) = \sum_i \sum_j x_i x_j B_{ij} \quad (88.1)$$

for the second virial coefficient of a gas mixture would be given by Equation (81.2), with constants  $\epsilon_{ij}$  and  $\sigma_{ij}$  referring to the potential energy between a molecule of the  $i$ th kind and one of the  $j$ th kind. It has been found that this is indeed possible.

It was already pointed out in Section 11 that the rules

$$\begin{aligned} \sigma_{ij} &= (\sigma_{ii} + \sigma_{jj})/2 \\ \epsilon_{ij} &= (\epsilon_{ii}\epsilon_{jj})^{1/2} \end{aligned} \quad (88.2)$$

lead to a satisfactory prediction of the second virial coefficients of non-polar gas mixtures, as well as to a justification of the "combining rules" developed for the common semi-empirical equations of state. We shall not take space to describe comparisons with the experimental compressibility measurements, but will consider briefly the theoretical and other experimental evidence in favor of Equation (88.2).

The dispersion effect between two dissimilar molecules is given explicitly by Equation (72.9), (72.11), or (72.13), and one of these formulae should certainly be used if all the required parameters are available. They all give the inequality

$$C_{ij}^2 \leq C_{ii}C_{jj} \quad (88.3)$$

where  $C$  represents the coefficient of  $r^{-6}$  in the dispersion energy. The third column of Table VII shows that the quantities  $h\nu_0$  for a number of molecules are quite similar in magnitude. If they were all exactly the same, Equation (88.3) would become an equality, and we may therefore use a geometric-mean rule for  $C$  in the absence of other information.

There has been no detailed calculation of the repulsive forces between a pair of unlike molecules, but empirical study of lattice distances in ionic crystals lends strong support to the simple idea that the effective diameters of spherically symmetrical ions or molecules are additive, as they would be for hard spheres. This would also be expected from the consideration that the magnitude of the repulsions is determined by the extent of overlapping of the electron-clouds of the two molecules. The additive rule of Equation (88.2) for  $\sigma_{ij}$  thus follows.

Recalling that  $C = 4\epsilon\sigma^6$  for the special Lennard-Jones function, and using the additive rule for  $\sigma_{ij}$ , we obtain another relation,

$$\epsilon_{ij}^2 \leq \epsilon_{ii}\epsilon_{jj} \quad (88.4)$$

which must involve an inequality greater than that of Equation (88.3), though still not a large one. However, it should be remembered that the second-order exchange forces may make some contribution in the region of the potential-energy minimum and that no theoretical information regarding this term is available. Therefore no exact theoretical statement can be made, and the attractive device of replacing Equation (88.4) by the geometric-mean rule of Equation (88.2) for  $\epsilon_{ij}$  must be tested by its empirical success. As applied to calculations of the thermodynamic properties of simple non-polar liquid solutions<sup>1</sup> and of the transport properties (diffusion and viscosity) of binary non-polar gas mixtures,<sup>2</sup> the geometric-mean rule generally provides a good approximation; and its failures, when appreciable, are almost always in the direction indicated by Equation (88.4). Available spectroscopic evidence also lends some support to this conclusion, the dissociation energies of the polarization-molecules HgA and HgXe lying fairly close to those predicted by the rule of the geometric mean.<sup>3</sup>

The situation in polar gas mixtures can be assessed with reference to the potential energy of Equation (83.1). The induction effect is small and follows Equation (71.4); therefore the rules of Equation (88.2) can be expected to hold equally well in this case. The orientation effect is proportional to the product  $\mu_i\mu_j$  of the two dipole moments, and hence vanishes if either molecule in a pair is non-polar. Thus the interactions between a polar and a non-polar molecule behave as though both molecules were non-polar. Straightforward application of these principles leads to the combining rules for polar gases given in Section 11.

<sup>1</sup> G. Scatchard, *Chem. Rev.*, **8**, 321 (1931); G. Scatchard, S. E. Wood, and J. E. Mochel, *J. Phys. Chem.*, **43**, 119 (1939).

<sup>2</sup> J. O. Hirschfelder, R. B. Bird, and E. L. Spotz, *Chem. Rev.*, **44**, 205 (1949).

<sup>3</sup> For pertinent references, plus a theoretical discussion of the forces in these molecules, see R. Heller, *J. Chem. Phys.*, **9**, 154 (1941).

# CHAPTER III

## THE LIQUID STATE

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### INTRODUCTION

While it is often said that a liquid is intermediate in its properties between a solid and a gas, this statement should not be understood to mean that every property of a liquid is intermediate in value between those of the other two states. If the actual figures are compared, it is found that in the great majority of cases the value of any property of a liquid is approximately equal either to that of the solid or to that of the gas. The intermediateness, then, is a statistical one—a liquid has some of the properties of a solid, and some of the properties of a gas.

The most obvious resemblance between liquids and gases is their lack of rigidity—neither offers permanent resistance to a shearing stress. The immediate consequence of this is that neither a liquid nor a gas possesses shape of its own, but always takes the shape of its container. Every solid,<sup>1</sup> on the other hand, possesses a definite crystalline form, and will always offer a resistance to shearing stress.

Between liquids and solids, the most prominent resemblance is that both possess cohesion, which enables each to maintain a free surface, whereas a gas will always completely fill any container. A second, and hardly less fundamental, property common to liquids and solids, is their relative incompressibility compared to gases. While the compressibilities of solids are usually of the order of  $10^{-6}$  atm<sup>-1</sup>, those of liquids are only slightly larger (about  $10^{-5}$  atm<sup>-1</sup>). The compressibility of a gas, on the other hand, is roughly equal to the reciprocal of the pressure, or, at a pressure of one atmosphere, about  $10^5$  times as great as that of a liquid. Closely allied to the second similarity between liquids and solids is the third: their similarity in density. The density change which takes place when a solid melts is usually of the order of 10 to 50 per cent, but on vaporization the density decreases by a factor of 100 or 1,000.

From these simple facts considerable information can be obtained about the nature of the molecular arrangement in liquids. From the density, for example, the mean distance between molecules can be calculated. Taking argon as a typical example, the molar volumes of the solid, liquid and gas at the boiling point are respectively 24.3 cc, 28.1 cc, and 7,050 cc. As a first crude

<sup>1</sup> Throughout this chapter the word "solid" will always refer to crystalline solids, and not to glasses or other amorphous solids.



hypothesis for the molecular arrangement we might assume that the molecules of the liquid and gas are arranged like those of the solid in a face-centered cubic lattice. To obtain the correct densities it is then necessary to assume that the distance between nearest neighbors is 3.84 Å in the solid, 4.03 Å in the liquid and 25.4 Å in the gas. These three lattices are shown in Fig. 1. In the solid the molecules are in contact.

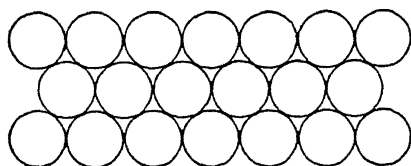
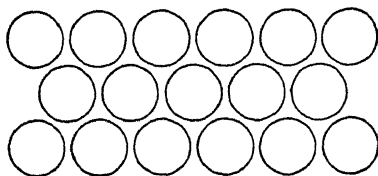
*Solid**Liquid**Gas*

FIG. 1. Relative Spacing of Molecules in Solid, Liquid and Gaseous Phases. Note: This diagram is intended to show only the relative spacings, and not the actual configurations.

(about 5 per cent of the molecular diameter) between molecules. In the gas the space between molecules is about six times the molecular diameter.

Since the forces between molecules are short range forces, and act through a distance of only two or three times the molecular diameter, it is immediately obvious that in the gas these forces are of little importance. Any such regular arrangement of molecules as that we have assumed will therefore be destroyed by the thermal motions of the molecules, and the usual assumption that the molecules of a gas are arranged in space at random is justified.

In the solid, on the other hand, the close-packed arrangement of the molecules prevents any molecule from moving far from its original position, which results in turn in the rigidity of the crystal. At the same time the low compressibility of the solid is due

to the fact that there is no free space between the molecules, so that any compression must be accomplished by reducing the size of the molecules themselves.

If the liquid maintains the arrangement we have assumed, it is difficult to see how to explain its fluidity. The molecules are packed so closely together that no interior molecule can change its position by much more than can the molecule of the solid. The only conceivable way in which flow could take place would be by the simultaneous displacement of a whole plane of molecules. Such a motion, however, would require the simultaneous lengthening of a great number of intermolecular distances, and hence a large energy of activation for the flow process. To avoid this difficulty it is obviously necessary to assume that a few molecules move at a time, but this in turn implies that it must be relatively easy for molecules to become displaced from the regular lattice.

On the other hand, the problem of packing so many spheres into a given volume does not permit any great variation from the regular close-packed

structure. In fact, the only reasonable modifications which can be made are two in number. First, there may be local irregularities caused by groups of molecules coming closer together, leaving wider spaces elsewhere in the structure. Second, there may be a gradual distortion of the structure as we go from molecule to molecule, so that although the pattern in the immediate neighborhood of a given molecule may be quite regular, the pattern is irregular at a distance.

(1) **X-ray Diffraction in Liquids:** These conclusions have found direct confirmation in the study of the X-ray diffraction patterns of liquids. Unlike solids, which give a characteristic pattern of Laue spots when a beam of X-rays is passed through a crystal, the diffraction pattern of a liquid is a series of light and dark rings. It has been shown<sup>1</sup> that, by a Fourier analysis of this pattern, one can calculate directly the radial distribution of atoms surrounding any average atom. If  $\rho(r)$  is the average number of atoms per unit volume at a distance  $r$  from a given atom,  $\rho_0$  is the average number of atoms per unit volume for the whole liquid, and  $I$  is the intensity of the unmodified scattering in electron units per molecule at the angle  $\theta$  to the original beam, then<sup>2</sup>

$$4\pi r^2 \rho(r) = 4\pi r^2 \rho_0 + \frac{2r}{\pi} \int_0^\infty si(s) \sin rs ds \quad (1.1)$$

where  $s = (4\pi/\lambda) \sin \theta$ ,  $\lambda$  is the wavelength of the X-rays, and

$$i(s) = I/f^2 - 1 \quad (1.2)$$

$f$  being the atomic scattering factor.<sup>3</sup> Analyses of this type have been made for a number of liquids. The curve obtained for liquid sodium by Tarasov and Warren<sup>4</sup> is shown in Fig. 2. In this figure  $4\pi r^2 \rho(r)$ , the number of atoms in a spherical shell of unit thickness at a distance  $r$  from an arbitrary central atom, is plotted against  $r$ . From this diagram it is seen that there are no atoms whose centers lie nearer than about 3 Å to the central atom, as we might expect from even the crudest conception of a liquid consisting of impenetrable spheres. At a distance of about 4 Å, on the other hand, there is a definite concentration of atoms, higher than one would expect if the centers of the atoms were scattered at random. The area under this first hump in the curve shows that there are about ten neighboring atoms at this distance.<sup>5</sup> This number is not far from the number (12) of spheres arranged around a central sphere in closest packing. At a slightly larger distance (around 5 Å) the number of atoms again falls below the expected number and then rises once more above the random density at about 7 Å.

<sup>1</sup> F. Zernike and J. A. Prins, *Z. Physik*, **41**, 184 (1927); P. Debye and H. Menke, *Ergeb. tech. Röntgenkunde*, II.

<sup>2</sup> For a derivation of this equation see B. E. Warren, *J. Applied Phys.*, **8**, 645 (1937).

<sup>3</sup> A. H. Compton and S. K. Allison, *X-rays in Theory and Experiment* (New York: D. Van Nostrand Co., Inc., 1935), pp. 781–782.

<sup>4</sup> L. P. Tarasov and B. E. Warren, *J. Chem. Phys.*, **4**, 236 (1936).

<sup>5</sup> F. H. Trimble and N. S. Gingrich, *Phys. Rev.*, **53**, 278 (1938).

Sodium crystallizes in a body-centered cubic lattice. An atom in the solid has, therefore, eight nearest neighbors which lie at a distance of 3.72 Å. These eight neighbors are in turn surrounded by six at a distance of 4.30 Å from the central atom, and so on. These "shells" of atoms are represented in Fig. 2 by

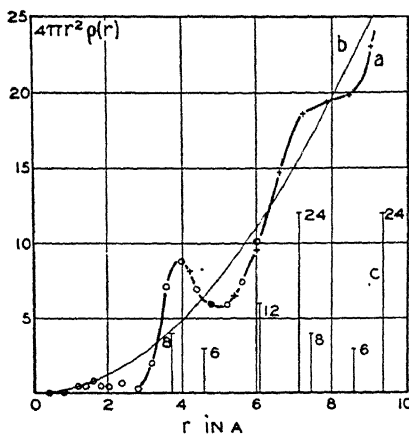


FIG. 2. (a) Radial distribution curve for liquid sodium  $4\pi r^2 \rho(r)$ ; (b) Average density curve  $4\pi r^2 \rho_0$ ; (c) Distribution of neighbors in crystalline sodium.

vertical lines of a height proportional to the number of atoms in the shell. The resemblance between the liquid density curve and the solid structure is very marked, and it is evident that the liquid structure must be a rather irregular version of the solid structure, at least over distances of the order of a few atomic diameters.

The results of similar X-ray studies of other liquids are of the same general nature. A particularly interesting case is that of water, which has been studied extensively.<sup>6</sup> The X-ray pattern of water shows that each water molecule is surrounded by only four neighboring molecules, which are at a distance slightly greater than that between nearest neighbors in ice. In the solid each oxygen atom is joined

to four other oxygen atoms by "hydrogen bonds" arranged tetrahedrally.<sup>6</sup> Bernal and Fowler have suggested that these hydrogen bonds are preserved to some extent in the liquid. In order to account for the increase in density on melting, they assumed that the intermolecular distance was smaller in the liquid than in the solid, the shift being analogous to one from a tridymite-like structure to a quartz-like structure. The work of Morgan and Warren,<sup>6</sup> however, is inconsistent with this idea, for they found that the intermolecular distance *increased* on melting. In order to explain the increase in density it is therefore necessary to assume that the number of near neighbors increases. This is possible because of the fact that the ice does not have a close-packed structure. The four water molecules surrounding a given oxygen atom in ice by no means completely fill the surrounding space, so that other molecules can slip into the holes which are empty in ice. Since oxygen has a coordination number of four, these foreign molecules cannot be held to the oxygen by covalent bonds, so that such a structure is less orderly than the ice structure and hence should have a higher entropy.

We may, therefore, picture the melting of ice as a partial breaking of the ice structure, with the breaking of a portion of the hydrogen bonds. The

<sup>6</sup> G. W. Stewart, *Phys. Rev.*, **37**, 9 (1931); E. Amaldi, *Physik. Z.*, **32**, 914 (1931); H. H. Meyer, *Ann. Physik*, **5**, 701 (1930); S. Katzoff, *J. Chem. Phys.*, **2**, 841 (1934); J. D. Bernal and R. H. Fowler, *ibid.*, **1**, 515 (1933); J. Morgan and B. E. Warren, *ibid.*, **6**, 666 (1938).

resulting fragments tend to pack together as closely as possible, so that some of the oxygen atoms acquire more than their normal quota of four nearest neighbors. The heat of fusion is used up in breaking the hydrogen bonds, while approach to closest packing causes the increase in density.

With further heating the density is subject to two opposing influences. First, the breaking-up of the ice structure continues, leading to still closer packing and a greater density. Second, the thermal agitation tends to increase the intermolecular distances, thereby decreasing the density. At higher temperatures the second effect predominates over the first and the density decreases.

(2) **Short and Long Range Order:** The tendency of a liquid molecule to surround itself with a more or less definite number of neighboring molecules at or near a definite distance shows that if we consider a region in the liquid so small that it contains only a few molecules—say about 20—these molecules must be arranged very nearly in as regular a fashion as in the corresponding crystal. On the other hand, if the size of the region is enlarged, the irregularities mount up, and the positions of the molecules no longer can be related to a lattice of the type occupied by the molecules in the crystal. The regularity exhibited by the crystal is now generally referred to as *long range order*, since the positions of molecules many diameters away from a central molecule can be predicted from a knowledge of the position of the central molecule and the molecules immediately surrounding it.

In the liquid, on the other hand, this long range order has disappeared. Nevertheless, since the arrangement of the molecules immediately surrounding the central atom is reasonably definite, we can say that the liquid still possesses *short range order*. The crystal, of course, has short range order as well as long range order, but in the gas phase even the short range order has disappeared.

We can, therefore, state as an experimental fact that the melting of a crystal is accompanied by the disappearance of long range order, and the evaporation of a liquid is accompanied by the disappearance of short range order.

(3) **Holes:** The results of X-ray diffraction studies on liquids establish another important characteristic of liquid structure. The area under the first peak in the radial distribution function is almost always smaller than the number of neighbors in the crystal at or near this distance. For example, in the case of sodium discussed above, the area under the first peak corresponds to about ten neighbors. In the range covered by this peak, the solid has eight nearest neighbors and six more next nearest neighbors at an only slightly greater distance. Hence, about four of the 14 neighboring atoms about a central atom in the solid are missing in the liquid. In other words, there are definite gaps in the packing of the atoms. These gaps or *holes* may also be present in crystals, but in much smaller numbers. In fact, their presence in the solid state was realized before their role in the liquid state was formulated.<sup>1</sup> The presence of these holes affords an opportunity, which would not be available otherwise, for the molecules of the liquid to move about. In fact, it seems

<sup>1</sup> A. Joffe, *Ann. Physik*, 72, 461 (1923); J. Frenkel, *Z. Physik*, 35, 652 (1926).

almost obvious that the fluidity of the liquid state depends directly on their presence.

It should be noted that the decrease in density in the melting process is only partly accounted for by hole formation. The remainder arises from the increase in the average distance between nearest neighbors.

(4) **The Loose Packing of Rigid Spheres:** Many of the features of liquids are shown by a simple collection of rigid spheres. If the spheres are packed carefully to make the volume occupied a minimum, then a regular crystal-like lattice—either hexagonal or cubic—is formed. But if the volume available to the spheres is greater than that required for close packing, the regularity of the structure will disappear. This has been demonstrated in two dimensions by a number of experimenters<sup>1</sup> who have studied the distribution of spheres and other objects distributed on a flat surface. The three dimensional problem has been studied experimentally by Morrell and Hildebrand<sup>2</sup> by suspending hard gelatin spheres in a solution of the same density. These experiments gave radial distribution curves which were extremely close to those obtained by X-ray diffraction in liquids.

It would appear from this experimental evidence that the principal factor in the determination of the radial distribution function in a liquid is the volume occupied by the molecules themselves, that is to say, the repulsive forces between the molecules rather than their attraction.

(5) **Theory of Loose Packing in One Dimension:** In order to understand the theoretical problems involved in making a theoretical calculation of the loose packing of spheres, let us consider the problem in one dimension,<sup>3</sup> where a simple and exact solution can be obtained. We take up first the random distribution of  $N$  points on a line of length  $L$ . In any interval of length  $dx$ , the probability of one of our points falling in the interval is  $(N/L)dx$ . In a finite interval of length  $x$  the expected number of points is  $Nx/L$ . The probability of exactly  $k$  points in such an interval is easily seen to be

$$\frac{N!}{k!(N-k)!} \left(\frac{x}{L}\right)^k \left(1 - \frac{x}{L}\right)^{N-k} \quad (5.1)$$

which becomes the Poisson law<sup>4</sup>

$$\frac{\left(\frac{Nx}{L}\right)^k e^{-\frac{Nx}{L}}}{k!} \quad (5.2)$$

if  $N$  is large and  $x/L$  is small. In particular, the probability of finding no points in the interval is  $e^{-\frac{Nx}{L}}$ . Consider such an interval taken with one of

<sup>1</sup> H. Menke, *Physik. Z.*, **33**, 593 (1932); J. A. Prins, *Naturwissenschaften*, **19**, 435 (1931).

<sup>2</sup> W. E. Morrell and J. H. Hildebrand, *J. Chem. Phys.*, **4**, 224 (1936).

<sup>3</sup> J. Frenkel, *Kinetic Theory of Liquids* (New York: Oxford University Press, 1946), p. 126.

<sup>4</sup> T. C. Fry, *Probability and Its Engineering Uses* (New York: D. Van Nostrand Co., Inc., 1928), p. 214.

the points at its left end. The probability that the  $k$ th point to the right of the chosen point falls in an interval  $dx$  at the end of the interval  $x$  is just the product of the probability of finding  $k - 1$  points in the interval  $x$  and the probability of a point in the interval  $dx$ , or

$$\left(\frac{N}{L}\right)^k \frac{x^{k-1} e^{-Nx/L}}{(k-1)!} dx \quad (5.3)$$

Now let us turn to the distribution of spheres on a line. If the diameter of each sphere is  $a$ , then the  $N$  spheres occupy a length  $Na$ , leaving a length  $l = L - Na$  to be distributed in the form of gaps between the spheres. This distribution can be made by taking a random distribution of  $N$  points on a line of length  $l$ , and using the intervals between the points as the lengths of the gaps between the spheres.

If we start from the center of any given sphere, the chance of finding the  $k$ th sphere to the right at a distance  $x$  is equal to the chance that in the corresponding point distribution the  $k$ th point is at a distance  $x - ka$  (provided of course that  $x > ka$ ), or

$$\left(\frac{N}{l}\right)^k \frac{(x - ka)^{k-1} e^{-N(x-ka)/l}}{(k-1)!} dx \quad (5.4)$$

The total probability of finding the center of *any* molecule at a distance  $x$  is therefore

$$\rho(x)dx = \sum_{k=1}^{x/a} \left(\frac{N}{l}\right)^k \frac{(x - ka)^{k-1} e^{-N(x-ka)/l}}{(k-1)!} dx \quad (5.5)$$

The contribution of the  $k$ th term in this series to  $\rho(x)$  is zero for all values of  $x$  less than  $ka$ . The term then increases with further increase of  $x$  until it reaches a maximum at  $x = ka + \frac{(k-1)l}{N}$  with an approximate value  $N/l$ . It then decreases exponentially to zero. The distribution function therefore consists of a series of equally spaced peaks of more or less uniform height, at intervals of  $a + \frac{l}{N}$ . If the length of the line is decreased, the peaks become higher and sharper until at  $L = Na$  the distribution finally becomes close-packed.

**(6) Theory of Loose Packing in Three Dimensions:** In three dimensions it has not yet been possible to derive an exact form for the radial distribution function for loose-packed spheres. The following approach is due to Kirkwood.<sup>1</sup> In spite of its approximate nature, it gives results in good agreement with experiment.

We consider  $N$  rigid spheres of diameter  $a$  in a volume  $V$ . We wish to calculate the average density (number per unit volume) of spheres at a distance  $R$  from the center of an arbitrarily chosen central sphere. Let us consider

<sup>1</sup> J. G. Kirkwood and E. M. Boggs, *J. Chem. Phys.*, 10, 394 (1942).

the possibility of adding one more sphere to our collection. In order to find a place in which to place this sphere we must locate a hole in the distribution of sufficient size to accommodate the newcomer. The probability of finding such a hole will depend on the distance from our central sphere at which we look for it. For example, the center of the hole cannot be located nearer the central sphere than the diameter  $a$ . Let  $P(R)$  be the probability that if a point is chosen at a distance  $R$  from the center of the central sphere, a hole exists around the chosen point large enough to accommodate the new sphere with its center at the chosen point.

We may now assume that when the new sphere is added, it is equally likely to be added at any of the points at which a hole exists. The probability that it is placed in a volume element at a distance  $R$  from the central sphere is therefore proportional to  $P(R)dv$ . But, in the new assembly, the newly added sphere is distinguished in no way from the other spheres. The probability that *any* sphere is to be found at a distance  $R$  from the central sphere must be proportional to  $P(R)dv$ . In other words, the probability of finding a molecule at any point is proportional to the probability of finding a hole at that point.

If this last statement seems paradoxical, consider a very dense system in which all the spheres are on, say, a cubic close packed lattice, but with a small fraction  $\alpha$  of the lattice sites unoccupied. If we take any point which is not a lattice point the probability of finding a sphere with center at the point is zero, but the probability of finding a hole, that is, of placing a new sphere at that point, also vanishes. At the lattice points, on the other hand, there is a probability  $1 - \alpha$  of finding the point occupied by a sphere, and a probability  $\alpha$  of finding a hole. Hence at *any* point, the probability of finding a sphere is  $(1 - \alpha)/\alpha$  times the probability of finding a hole.

We now consider the calculation of  $P(R)$ . If we consider a spherical region of radius  $a$  and volume  $\omega = \frac{4}{3}\pi a^3$  with its center at a distance  $R$  from the center of our central sphere, then the expected number of spheres whose centers lie within  $\omega$  is

$$\epsilon(R) = \int_{\omega} \rho(r) dv \quad (6.1)$$

where it should be noted that  $r$  is measured to the center of the central sphere, not to the center of the spherical region under consideration. To a first approximation we can put

$$P(R) = 1 - \epsilon(R) \quad (6.2)$$

although this may break down if  $\epsilon(R)$  becomes nearly unity, since  $P(R)$  must remain positive. The proportionality between  $P(r)$  and  $\rho(r)$  then leads to the equation

$$\rho(R) = \text{const} [1 - \epsilon(R)] \quad (6.3)$$

To evaluate the constant we note that, at very large  $R$ ,  $\rho(R)$  must approach  $\rho_0$ , the density of the spheres in the whole volume. Hence

$$\epsilon(R) = \omega \rho_0 \quad (6.4)$$

so that

$$\rho_0 = \text{const} (1 - \omega \rho_0) \quad (6.5)$$

Eliminating the constant gives

$$\frac{\rho(R)}{\rho_0} = \frac{1 - \epsilon(R)}{1 - \omega \rho_0} \quad (6.6)$$

or, writing out  $\epsilon(R)$

$$\frac{\rho(R)}{\rho_0} = \frac{1}{1 - \omega \rho_0} - \frac{1}{1 - \omega \rho_0} \int_{\omega}^R \rho(r) dv \quad (6.7)$$

We have thus found an integral equation which must be satisfied by  $\rho(R)$  for all values of  $R$  greater than  $a$ . For smaller values of  $R$ ,  $\rho(R)$  must of course vanish.

Equation (6.7) takes the form

$$\frac{\rho(R)}{\rho_0} = \frac{1}{1 - \omega \rho_0} - \frac{1}{1 - \omega \rho_0} \frac{\pi}{R} \int_{R-a}^{R+a} [a^2 - (R - r)^2] r \rho(r) dr \quad (6.8)$$

when the volume integral has been expressed in bipolar coordinates and integrated once. In this equation put

$$\lambda = 1 - \omega \rho_0 \quad (6.9)$$

$$R = ax \quad (6.10)$$

$$r = as \quad (6.11)$$

$$\rho(R) = \rho_0 \left( 1 + \frac{\varphi(x)}{x} \right) \quad (6.12)$$

Then, after a little reduction,

$$\varphi(x) = -\frac{\lambda}{4} \int_{x-1}^{x+1} [1 - (x - s)^2] \varphi(s) ds \quad (6.13)$$

is the equation which must be satisfied by  $\varphi(x)$  when  $x > 1$ , while for  $0 < x < 1$  we must have  $\varphi(x) = -x$ .

It is easily seen that the solution of this equation must be oscillatory in character. For, suppose that  $\varphi(x)$  was positive from  $x_0 - 1$  to  $x_0 + 1$ . Then  $\varphi(x_0)$  would be positive, while the right side of the equation would be negative. It follows that in any interval of length 2,  $\varphi(x)$  must take both positive and negative values.

By substitution in the integral equation we find that there are solutions of the form

$$\varphi(x) = ce^{zx} \quad (6.14)$$



provided that  $z$  satisfies the equation

$$\frac{z \cosh z - \sinh z}{z^3} = -\frac{1}{\lambda} \quad (6.15)$$

For real  $z$ , the left side of this equation is always positive, so that  $z$  must be a complex number, corresponding to the oscillatory character of the solution already established.

Now let us put  $z = -\alpha + i\beta$  ( $\alpha, \beta$  real) and suppose that  $\alpha$  (but not  $\beta$ ) is large. Then approximately

$$\frac{z \cosh z - \sinh z}{z^3} = \frac{e^z}{z^2} = \frac{e^\alpha (\cos \beta + i \sin \beta)}{\alpha^2} \quad (6.16)$$

For this to be a negative real number we must have  $\sin \beta = 0$ ,  $\cos \beta < 0$ , which requires that

$$\beta = (2n + 1)\pi \quad (n = 0, 1, 2, \dots) \quad (6.17)$$

For this  $\beta$  we must have

$$\frac{e^\alpha}{\alpha^2} = \frac{1}{\lambda} \quad (6.18)$$

which can be satisfied with large  $\alpha$  if  $\lambda$  is small. There is also a solution with  $\alpha$  large and negative but this solution corresponds to oscillations in  $\varphi$  and hence in  $\rho(R)$  which grow larger and larger as the distance from the central molecule is increased. Hence this solution is not suitable for our purposes.

The acceptable solution for small values of the density is, therefore, of the form

$$\varphi(x) = e^{-\alpha x + i\beta x} \quad (6.19)$$

or, taking the real part,

$$\varphi(x) = e^{-\alpha x} \cos \beta x \quad (6.20)$$

and

$$\rho(R) = \rho_0 \left( 1 + \frac{a}{R} e^{-\alpha R/a} \cos \beta R/a \right) \quad (6.21)$$

We have, therefore, a damped-wave form of the radial distribution function, with a wavelength

$$\frac{2\pi a}{\beta} = \frac{2a}{(2n + 1)} \quad (6.22)$$

The fundamental wavelength ( $n = 0$ ) is  $2a$ , and the others correspond to the odd harmonics. The damping factor is

$$\frac{\alpha}{a} = \frac{1}{\ln \frac{1}{\lambda} a} \quad (6.23)$$

approximately, so that the waves of density fall to  $e^{-1}$  of their initial value in a distance  $a \ln \frac{1 - \omega\rho_0}{3\omega\rho_0}$ . As the density (and hence  $\lambda$ ) is increased, the smallest value of  $\beta$  increases and  $\alpha$  decreases, until, when  $\lambda = 34.8$ ,  $\alpha$  vanishes. At this point, where  $\omega\rho_0 = 0.920$ , the system acquires undamped oscillations in the density. Such oscillations correspond to the onset of long range order. It should be noted that at the point where this occurs the system is a long way from being close packed, for  $\omega\rho_0$  in a close-packed system is  $4\pi\sqrt{2}/3 = 5.9$ .

The numerical value of the density at which long range order sets in should not be trusted too greatly. The theory on which it was derived contains several approximations which may very well break down at high densities. The most important of these is the relationship between the expected number of molecules in the volume of a hole and the probability of occurrence of the hole. We have taken this to be

$$P(R) = 1 - \epsilon(R) \quad (6.2)$$

which is certainly correct if  $\epsilon(R)$  is small, that is, at low densities. But at higher densities this relationship must be false, since  $\epsilon(R)$  may become greater than unity, while  $P(r)$  must remain positive. If the spheres could be assumed to be distributed at random, the relationship would be

$$P(R) = e^{-\epsilon(R)} \quad (6.24)$$

This would lead to the modified integral equation

$$\ln \frac{\rho(R)}{\rho_0} = \omega\rho_0 - \int_{\omega} \rho(r) dv \quad (6.25)$$

It has been proposed that this would be a better approximation than Equation (6.7), but this is doubtful, since the assumption that the spheres are placed at random can not be justified. Furthermore, the solution of such an inhomogeneous integral equation presents great difficulties.

We may, however, expect that the solution we have obtained is qualitatively correct in the conclusion that even in the case of rigid spheres the radial distribution is similar to that found in liquids, and that long range order sets in at some critical density.

**(7) The Radial Distribution Function for Central Forces:** We now turn to the case of molecules subject to forces which depend only on the distance between the centers of the molecules, and which fall sufficiently rapidly to zero as the distance between centers becomes large. We shall assume that these forces are derivable from a potential energy function  $\varphi(r_{ij})$  where  $r_{ij}$  is the distance between the centers of the  $i$ th and  $j$ th molecules. The total potential energy of the system is then

$$\Phi = \frac{1}{2} \sum_{ij} \varphi(r_{ij}) \quad (7.1)$$

The general theory of such a system has been developed to the greatest extent by Kirkwood,<sup>1</sup> Mayer,<sup>2</sup> and Born and Green.<sup>3</sup> We shall here follow a method which resembles most closely that of Born and Green.

Let us consider  $N$  molecules in a volume  $V$ . If we consider an element of volume  $dv_1$ , there will be a certain probability that there is a molecule in the system whose center lies in  $dv_1$ . This we denote by  $\rho_1 dv_1$ . If the system is crystalline this probability may depend on the location of  $dv_1$ , but in fluid systems we shall be able to put

$$\rho_1 = \frac{N}{V} \quad (7.2)$$

We may likewise consider two elements of volume  $dv_1$  and  $dv_2$ . The probability that there are molecules with centers in both  $dv_1$  and  $dv_2$  we shall denote as  $\rho_2 dv_1 dv_2$ . If the molecules were randomly placed we should have

$$\rho_2 = \frac{N(N-1)}{V^2} \quad (7.3)$$

In general, however,  $\rho_2$  will depend on the coordinates of the volume elements  $dv_1$  and  $dv_2$ , and will vanish if  $dv_1$  and  $dv_2$  are very close together, because of the repulsive forces between the molecules.

We shall put  $\rho_n dv_1 \cdots dv_n$  for the probability that there are molecules in each of the  $n$  volume elements  $dv_1, dv_2, \dots, dv_n$ . The value of  $\rho_n$  will usually depend on the coordinates of the  $n$  volume elements. When it is necessary to distinguish various sets of these coordinates we shall write  $\rho_n(1, 2, 3, \dots, n)$ .

To calculate the various  $\rho_n$ , we apply the Boltzmann distribution law. If we consider all the possible configurations of the  $N$  molecules, the probability of the system being in any given configuration, defined by the requirement that molecule one lie in the volume element  $dv_1$ , etc., is

$$\text{const } e^{-\Phi/kT} dv_1 \cdots dv_N$$

The probability that  $n$  specified molecules be located in the  $n$  volume elements  $dv_1 \cdots dv_n$  is the sum of the probabilities of all the configurations which have the specified molecules so located, i.e.

$$\text{const } dv_1 \cdots dv_n \int \cdots \int e^{-\Phi/kT} dv_{n+1} \cdots dv_N$$

But since the  $n$  molecules must be somewhere in the system the integral

$$\text{const } \int \cdots \int e^{-\Phi/kT} dv_1 \cdots dv_N$$

<sup>1</sup> J. G. Kirkwood *et al.*, *J. Chem. Phys.*, **3**, 300 (1935); **7**, 919 (1939); **9**, 514 (1941); **10**, 394 (1942); **14**, 180 (1946).

<sup>2</sup> J. E. Mayer *et al.*, *J. Chem. Phys.*, **5**, 67 (1937); **6**, 101 (1938); **10**, 629 (1942); **13**, 276 (1945); **15**, 187 (1947). See also B. Kahn and G. Uhlenbeck, *Physica*, **5**, 399 (1938); M. Born, *Physica*, **4**, 1034 (1937); M. Born and K. Fuchs, *Proc. Roy. Soc.*, **A166**, 391 (1938).

<sup>3</sup> M. Born and H. S. Green, *Nature*, **159**, 251 (1947); *Proc. Roy. Soc.*, **A188**, 10 (1946); **A189**, 103 (1947).

must have the value unity. We conclude that the required probability is

$$\frac{dv_1 \cdots dv_n \int \cdots \int e^{-\Phi/kT} dv_{n+1} \cdots dv_N}{\int \cdots \int e^{-\Phi/kT} dv_1 \cdots dv_N}$$

To find the probability of *any*  $n$  molecules being found in  $dv_1 \cdots dv_n$  this must be multiplied by the number of ways of assigning molecules to the volume elements, or  $N(N-1) \cdots (N-n+1) = N!/(N-n)!$ . Hence

$$\rho_n = \frac{N!}{(N-n)!} \frac{\int \cdots \int e^{-\Phi/kT} dv_{n+1} \cdots dv_N}{\int \cdots \int e^{-\Phi/kT} dv_1 \cdots dv_N} \quad (7.4)$$

If we define

$$\Omega_n(1, 2, 3, \dots, n) = \int \cdots \int e^{-\Phi/kT} dv_{n+1} \cdots dv_N \quad (7.5)$$

Then

$$\rho_n = \frac{N!}{(N-n)!} \frac{\Omega_n}{\Omega_0} \quad (7.6)$$

We thus have a formal solution to the problem of finding  $\rho_n$ , but not one of practical use as yet. We note next that

$$\begin{aligned} \int \rho_{n+1}(1, 2, 3, \dots, n+1) dv_{n+1} \\ = \frac{N!}{(N-n-1)! \Omega_0} \int \cdots \int e^{-\Phi/kT} dv_{n+1} \cdots dv_N \\ = \frac{N!}{(N-n-1)!} \frac{\Omega_n}{\Omega_0} \\ = (N-n) \rho_n \end{aligned} \quad (7.7)$$

so that from a knowledge of any  $\rho_n$  we can find  $\rho_m$  if  $m < n$ .

We now consider the effect on  $\rho_n$  of a change in the position of one of the volume elements, say  $dv_1$ . For a change in the  $x$  direction

$$\begin{aligned} \frac{\partial \rho_n(1, 2, \dots, n)}{\partial x_1} &= \frac{N!}{(N-n)! \Omega_0} \frac{\partial \Omega_n(1, 2, \dots, n)}{\partial x_1} \\ &= \frac{N!}{(N-n)! \Omega_0} \int \cdots \int \frac{\partial}{\partial x_1} (e^{-\Phi/kT}) dv_{n+1} \cdots dv_N \\ &\quad \times \frac{N!}{kT (N-n)! \Omega_0} \sum_{j=1}^N \int \cdots \int \frac{\partial \varphi_{ij}}{\partial x_1} e^{-\Phi/kT} dv_{n+1} \cdots dv_N \end{aligned} \quad (7.8)$$

Of the terms in this summation, the term  $j = 1$  vanishes since there is no  $\varphi_{11}$ . The terms  $j = 2, 3, \dots, n$  do not involve the variables of integration and the factor  $\partial\varphi_{ij}/\partial x_1$  can be taken outside the integral. The remaining terms are all equal since the variables of integration can be permuted without affecting the integral. Hence

$$\frac{\partial\rho_n}{\partial x_1} = -\frac{1}{kT} \frac{N!}{(N-n)! \Omega_0} \left\{ \sum_{j=2}^n \frac{\partial\varphi_{1j}}{\partial x_1} \int \dots \int e^{-\Phi/kT} dv_{n+1} \dots dv_N \right. \\ \left. + (N-n) \int \dots \int \frac{\partial\varphi_{1,n+1}}{\partial x_1} e^{-\Phi/kT} dv_{n+1} \dots dv_N \right\} \quad (7.9)$$

This can be written

$$\frac{\partial\rho_n}{\partial x_1} = -\frac{1}{kT} \frac{N!}{(N-n)! \Omega_0} \left\{ \sum_{j=2}^n \frac{\partial\varphi_{1j}}{\partial x_1} \Omega_n \right. \\ \left. + (N-n) \int \frac{\partial\varphi_{1,n+1}}{\partial x_1} \Omega_{n+1} dv_{n+1} \right\} \\ = -\frac{\rho_n}{kT} \sum_{j=2}^n \frac{\partial\varphi_{1j}}{\partial x_1} - \int \frac{1}{kT} \frac{\partial\varphi_{1,n+1}}{\partial x_1} \rho_{n+1} dv_{n+1} \quad (7.10)$$

In particular

$$\frac{\partial\rho_2(12)}{\partial x_1} = -\frac{\rho_2(12)}{kT} \frac{\partial\varphi_{12}}{\partial x_1} - \int \frac{1}{kT} \frac{\partial\varphi_{13}}{\partial x_1} \rho_3(123) dv_3 \quad (7.11)$$

Since  $\varphi_{13}$  depends only on  $r_{13}$ , it is easily seen that

$$\frac{\partial\varphi_{13}}{\partial x_1} = -\frac{\partial\varphi_{13}}{\partial x_3}$$

Hence

$$\frac{\partial\rho_2(12)}{\partial x_1} = -\frac{\rho_2(12)}{kT} \frac{\partial\varphi_{12}}{\partial x_1} + \int \frac{1}{kT} \frac{\partial\varphi_{13}}{\partial x_3} \rho_3(123) dv_3 \quad (7.12)$$

The first term on the right side of this equation expresses the effect of the force  $(-\partial\varphi_{12}/\partial x_1)$  exerted on the molecule in  $dv_1$  by the molecule in  $dv_2$ . The integral expresses the effect of the force exerted by the remaining molecules of the system.

The equations for  $\partial\rho_2(12)/\partial y_1$  and  $\partial\rho_2(12)/\partial z_1$  are similar. Combining these equations, the gradient of  $\rho_2(12)$  is

$$\nabla_1\rho_2(12) = -\frac{\rho_2(12)}{kT} \nabla_1\varphi_{12} + \int \frac{1}{kT} \rho_3(123) \nabla_3\varphi_{13} dv_3 \quad (7.13)$$

(8) **The Kirkwood Approximation:** The equation we have just obtained requires a knowledge of the distribution function  $\rho_3$  before it can be applied. If the molecules were randomly distributed we could write

$$\rho_3(123) = \rho_1(1)\rho_1(2)\rho_1(3) \quad (8.1)$$

This would, however, be a very poor approximation. A much better approximation is that called by Kirkwood the *superposition approximation*. This amounts to the assumption that the force on any molecule in any set of molecules in fixed positions is the sum of the forces which would be exerted on the given molecule if we neglect in turn all but one other molecule in the set. That is to say, if we are given a set of three molecules located in the volume elements  $dv_1, dv_2, dv_3$ , the force on the molecule in  $dv_1$  is the sum of the force which would be exerted on it if the molecule in  $dv_2$  were kept in place and the remaining molecules (including the molecule in  $dv_3$ ) were free to move, and the force which would be exerted if the molecule in  $dv_3$  were kept in place and the remaining molecules were free to move. Under this assumption, which we shall call the Kirkwood approximation,  $\rho_3$  can be expressed in terms of  $\rho_2$  by the equation

$$\rho_3(123) = \frac{\rho_2(12)\rho_2(23)\rho_2(31)}{\rho_1(1)\rho_1(2)\rho_1(3)} \quad (8.2)$$

that is, the probability (density) of finding molecules in the three volume elements  $dv_1 dv_2 dv_3$  is the product of the probabilities for the three volume elements. We note that if the molecules are distributed at random this equation is satisfied, but that it can also be satisfied when the molecules are not at random.

Introducing the Kirkwood approximation into Equation (7.13) we find

$$\nabla_1 \rho_2(12) = -\frac{\rho_2(12)}{kT} \nabla_1 \varphi_{12} + \frac{\rho_2(12)}{kT \rho_1^3} \int \rho_2(13) \rho_2(32) \nabla_3 \varphi_{13} dv_3 \quad (8.3)$$

provided we can assume  $\rho_1$  to be independent of position (fluid system). This gives us an integro-differential equation by means of which it should be possible to find  $\rho_2$ , given the density  $\rho_1$  and the potential energy function  $\varphi$ . Our next task is to put this equation in a more usable form.

Let us denote the distance between  $dv_1$  and  $dv_2$  by  $r$ , that between  $dv_1$  and  $dv_3$  by  $s$ , and that between  $dv_2$  and  $dv_3$  by  $t$ . These are related by the equation

$$t^2 = r^2 + s^2 - 2rs \cos \theta \quad (8.4)$$

where  $\theta$  is the angle at  $dv_1$  between the lines to  $dv_2$  and  $dv_3$ . Because of this  $t$  can range only between  $|r - s|$  and  $|r + s|$ .

If we regard for the moment  $dv_2$  as fixed and  $dv_1$  variable in position,  $\rho_2(12)$  will be a function of the position of  $dv_1$  which is symmetrical about the point at which  $dv_2$  is located. Its gradient  $\nabla_1 \rho_2(12)$  must, therefore, have a direction along the line joining  $dv_1$  and  $dv_2$  and a magnitude  $-\frac{d\rho_2(r)}{dr}$ . The parallel

component of  $\nabla_1 \varphi_{12}$  is  $-\frac{\partial \varphi(r)}{\partial r}$ , and that of  $\nabla_3 \varphi_{13}$  is  $\frac{\partial \varphi(s)}{\partial s} \cos \theta$ , or

$$\frac{\partial \varphi(s)}{\partial s} \frac{r^2 + s^2 - t^2}{2rs}.$$

To express the volume element  $dv_3$  in terms of  $ds$  and  $dt$ , let us suppose that in the plane of the three volume elements we take a cartesian coordinate system with  $dv_1$  at the origin and the  $x$ -axis through  $dv_2$ , so that the element  $dv_2$  is at the point  $(r, 0)$ . If  $dv_3$  is at  $(x, y)$ , then

$$s^2 = x^2 + y^2$$

$$t^2 = (x - r)^2 + y^2$$

Hence, we have,

$$2s \frac{\partial s}{\partial x} = 2x \qquad 2s \frac{\partial s}{\partial y} = 2y$$

$$2t \frac{\partial t}{\partial x} = 2(x - r) \qquad 2t \frac{\partial t}{\partial y} = 2y$$

Therefore, the Jacobian,

$$\frac{\partial(s, t)}{\partial(x, y)} = \begin{vmatrix} \frac{x}{s} & \frac{y}{s} \\ \frac{x-r}{t} & \frac{y}{t} \end{vmatrix} = \frac{ry}{st}$$

and

$$\frac{\partial(x, y)}{\partial(s, t)} = \frac{st}{ry} \quad (8.5)$$

In two dimensions the volume element would, therefore, be  $\frac{st}{ry} ds dt$ . But the position of  $dv_3$  can be rotated at will about the line joining  $dv_1$  and  $dv_2$ . The distance of  $dv_3$  from this line is  $y$ , so that in three dimensions we must introduce an additional factor  $2\pi y$ , and we obtain

$$dv_3 = \frac{2\pi}{r} st ds dt \quad (8.6)$$

With these results we can write our integro-differential equation in the form

$$\frac{\partial \rho_2(r)}{\partial r} + \frac{\rho_2(r)}{kT} \frac{\partial \varphi(r)}{\partial r} + \frac{2\pi \rho_2(r)}{kT \rho_1^3 r} \iint \rho_2(s) \rho_2(t) \frac{\partial \varphi(s)}{\partial s} \frac{r^2 + s^2 - t^2}{2rs} st dt ds \quad (8.7)$$

This can be written

$$\frac{d}{dr} \left[ \ln \rho_2(r) + \frac{\varphi(r)}{kT} \right] = - \frac{\pi}{\rho_1^3} \int_0^\infty \int_{|r-s|}^{|r+s|} \rho_2(t) \frac{r^2 + s^2 - t^2}{t} dt$$

$$\cdot \rho_2(s) \frac{\varphi'(s)}{kT} ds \quad (8.8)$$

If we define  $\rho_2(-t) = \rho_2(t)$ , then the integrand is an odd function of  $t$ . The lower limit of integration can then be changed to  $r - s$  since the integral from

$r - s$  to  $s - r$  of an odd function vanishes. If we now integrate the equation from  $r = r_1$  to  $r = r_2$  (with  $r_2 \gg r_1$ )

$$\begin{aligned} \ln \rho_2(r_2) + \frac{\varphi(r_2)}{kT} - \ln \rho_2(r_1) - \frac{\varphi(r_1)}{kT} \\ - \frac{\pi}{\rho_1^3} \int_{r_1}^{r_2} \int_0^\infty \int_{r-s}^{r+s} \rho_2(t) \frac{r^2 + s^2 - t^2}{r^2} dt d\rho_2(s) \frac{\varphi'(s)}{kT} ds dr \\ = - \frac{\pi}{\rho_1^3} \int_0^\infty \int_{r_1-s}^{r_1+s} \int_{r_1}^{r_1+s} \frac{r^2 + s^2 - t^2}{r^2} dr d\rho_2(t) dt d\rho_2(s) \frac{\varphi'(s)}{kT} ds \\ - \frac{\pi}{\rho_1^3} \int_0^\infty \int_{r_1+s}^{r_2-s} \int_{t-s}^{t+s} \frac{r^2 + s^2 - t^2}{r^2} dr d\rho_2(t) dt d\rho_2(s) \frac{\varphi'(s)}{kT} ds \\ - \frac{\pi}{\rho_1^3} \int_0^\infty \int_{r_2-s}^{r_2+s} \int_{t-s}^{r_2} \frac{r^2 + s^2 - t^2}{r^2} dr d\rho_2(t) dt d\rho_2(s) \frac{\varphi'(s)}{kT} ds \quad (8.9) \end{aligned}$$

Carrying out the integrations over  $r$

$$\begin{aligned} \ln \rho_2(r_2) + \frac{\varphi(r_2)}{kT} - \ln \rho_1(r_1) - \frac{\varphi(r_1)}{kT} \\ - \frac{\pi}{\rho_1^3} \int_0^\infty \int_{r_1-s}^{r_1+s} \frac{s^2 - (t - r_1)^2}{r_1} \rho_2(t) dt d\rho_2(s) \frac{\varphi'(s)}{kT} ds \\ + \frac{\pi}{\rho_1^3} \int_0^\infty \int_{r_2-s}^{r_2+s} \frac{s^2 - (t - r_2)^2}{r_2} \rho_2(t) dt d\rho_2(s) \frac{\varphi'(s)}{kT} ds \quad (8.10) \end{aligned}$$

In the first of the integrals on the right side of this equation put  $t + r_1$  in place of  $t$ ; in the second,  $t + r_2$ . Then

$$\begin{aligned} \ln \rho_2(r_2) + \frac{\varphi(r_2)}{kT} - \ln \rho_2(r_1) - \frac{\varphi(r_1)}{kT} \\ = - \frac{\pi}{\rho_1^3} \int_0^\infty \int_{-s}^s \frac{(s^2 - t^2)(t + r_1)}{r_1} \rho_2(t + r_1) dt d\rho_2(s) \frac{\varphi'(s)}{kT} \\ + \frac{\pi}{\rho_1^3} \int_0^\infty \int_{-s}^{r_2+s} \frac{(s^2 - t^2)(t + r_2)}{r_2} \rho_2(t + r_2) dt d\rho_2(s) \frac{\varphi'(s)}{kT} ds \quad (8.11) \end{aligned}$$

But for large values of  $r_2$  we must have  $\rho_2(r_2) = \rho_1^2$  and  $\varphi(r_2) = 0$ . Replacing  $r_1$  by  $r$  we finally obtain

$$\begin{aligned} \ln \frac{\rho_2(r)}{\rho_1^2} + \frac{\varphi(r)}{kT} \\ = \frac{\pi}{\rho_1^3} \int_0^\infty \int_{-s}^s (s^2 - t^2) \left[ \frac{t+r}{r} \rho_2(t+r) - \rho_1^2 \right] dt d\rho_2(s) \frac{\varphi'(s)}{kT} ds \quad (8.12) \end{aligned}$$

This non-linear equation is too difficult to solve exactly. It has, therefore,



been approximated by putting

$$\rho_2(r) = \rho_1^2 e^{-\varphi(r)/kT} [1 + f(r)] \quad (8.13)$$

and assuming that  $f(r) \ll 1$ . This leads to the equation

$$\begin{aligned} r f(r) = & -\pi \rho_1 \int_0^\infty \int_{-s}^s (s^2 - t^2)(t+r)f(t+r)[1 + \alpha(t+r)]dt \\ & \cdot \alpha'(s)[1 + f(s)]ds - \pi \rho_1 \int_0^\infty \int_{-s}^s (s^2 - t^2)(t+r) \\ & \cdot \alpha(t+r)d\alpha'(s)[1 + f(s)]ds \end{aligned} \quad (8.14)$$

where

$$\alpha(r) = e^{-\varphi(r)/kT} - 1 \quad (8.15)$$

For short range forces,  $\alpha(r)$  and  $\alpha'(r)$  are small except near  $r = 0$ . Hence, in integrals involving the product of  $f(r)$  with  $\alpha(r)$  or  $\alpha'(r)$ , we may replace  $f(r)$  by a constant  $\epsilon - 1$ . Then, after an integration by parts,

$$r f(r) = 2\pi \rho_1 \int_0^\infty \int_{-s}^s (t+r)[f(t+r) + \epsilon \alpha(t+r)]dt \epsilon \alpha(s)ds \quad (8.16)$$

If we now define  $g(r)$  and  $\beta(r)$  by

$$r g(r) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^\infty s f(s) \sin(rs) ds \quad (8.17)$$

$$r \beta(r) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^\infty s \alpha(s) \sin(rs) ds \quad (8.18)$$

and  $\lambda$  by  $\lambda^{-1} = (2\pi)^{3/2} \rho_1$ , we find

$$\lambda g(r) = [g(r) + \epsilon \beta(r)] \epsilon \beta(r) \quad (8.19)$$

and by the Fourier inversion theorem

$$r f(r) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^\infty \frac{\epsilon^2 s \beta(s) \sin(rs) ds}{\lambda - \epsilon \beta(s)} \quad (8.20)$$

This is a formal solution to the problem.

Except at small values of  $r$ ,  $\varphi(r)$  is negative and  $\alpha(r)$  is positive. At high temperatures  $\alpha(r)$  is small, but at low temperatures  $\alpha(r)$  becomes large. It follows that  $\beta(r)$  also becomes large at small temperatures. For a given  $\lambda$ , i.e., for a given density, the denominator  $\lambda - \epsilon \beta(s)$  in Equation (8.20) will be positive for all values of  $s$  provided the temperature is sufficiently high, but on lowering the temperature a point will be reached at which  $\lambda - \epsilon \beta(s)$  vanishes for a pair of values of  $s$ , say  $\pm s_0$ . At this temperature the integral becomes singular. The singularity can only be avoided by changing the path of integration from the real axis to a curve in the complex plane which detours around

the singular points. In the complex plane, however, an infinite number of paths of integration are formally possible. The functions  $f(r)$  obtained on different paths differ by terms of the form

$$\frac{A_k}{r} \sin(rs_k) \quad (8.21)$$

where the  $A_k$  are constants and the  $s_k$  are roots of the equation

$$\beta(s) = \frac{\lambda}{\epsilon} \quad (8.22)$$

The correct path is that which makes  $f(r)$  approach 0 sufficiently rapidly at large  $r$  to make the density calculated from the radial distribution function agree with that determined by  $\rho_1$ . Above and below the temperature at which the singularity appears on the real axis these paths are different. It follows that  $f(r)$ , and hence the radial distribution function changes discontinuously at this temperature.

It is very tempting to identify this discontinuity in the radial distribution function with the change of state from the gas to the liquid. However, the validity of this identification is still open to question. For one thing, the discontinuity has only been shown for the approximate linearized integral Equation (8.14). It may be that the exact equation has no such discontinuity in its solution.

Strange as it may seem, there is no such discontinuity in the radial distribution if a gas is cooled at constant volume. Such a cooling process does result eventually in the formation of a liquid as a separate phase, and in that phase there is a radial distribution function which does differ sharply from that of the gas. But the radial distribution function being calculated is *not* that for either phase, but for the entire system. This is the weighted average of the radial distribution functions of the two phases. In the actual cooling process the amount of liquid grows continuously from zero, and this weighted average never has a discontinuity.

In the case of rigid spheres, this method of attack reduces in its essentials to the method of Kirkwood already discussed. It is important to notice that in the calculation of the radial distribution function of argon the agreement with the radial distribution function obtained by X-ray diffraction was good, although the experimental function was obtained on the liquid, and the calculation was made using values of the parameters such that the temperature was above the temperature of the discontinuity. The nature of the temperature at which the solution of (8.20) becomes discontinuous is therefore still obscure.

(9) **The Hole Theory of Liquids:** Since the strict application of statistical mechanics has up to now failed to yield a complete theory of liquids, a number of attempts have been made to construct simplified models which are amenable to relatively simple mathematical development and yet represent to some extent at least the most important features of the liquid state.

In the cases of the gaseous and solid states it has long been customary to treat such idealized systems first and then to proceed to the consideration of departures of actual systems from the ideal. For liquids, on the other hand, no such ideal has been generally agreed upon, for a liquid has neither the perfect order of an ideal solid nor the complete disorder of an ideal gas.

Attempts have been made to use a model in which the liquid is considered to be an imperfect crystal—imperfect in the sense that not all the lattice sites of the crystal are occupied by molecules. The vacant sites correspond to the “holes” we have already discussed, and the theory based on this model is usually referred to as the hole theory.<sup>1</sup>

In order to use such a theory it must first be shown that the model is thermodynamically stable. Qualitatively, the formation of holes in a crystal lattice must be accompanied by an increase in energy because of the loss of the energy of attraction between the molecules. This increase in energy, however, is limited to the total binding energy of the crystal. As the number of holes is increased the energy should at first rise linearly with the number of holes, but eventually approach a constant value. For the holes to be stable, this increase in energy must be accompanied by an increase in the entropy. This can be attributed to the fact that, as the number of holes increases, the number of arrangements of the holes and molecules also increases.

The idea can be expressed mathematically by the following approximation. Suppose that each lattice site is surrounded by  $z$  nearest neighbors and that only the interactions between molecules on neighboring sites need be considered. If our system consists of a lattice with  $N$  molecules and  $N'$  holes, distributed at random so that each molecule has on the average  $zN/(N + N')$  molecules around it on neighboring sites, the energy of the system is

$$E = -\frac{1}{2}zU_0N \frac{N}{N + N'} \quad (9.1)$$

if  $-U_0$  is the interaction energy between nearest neighbors. The number of ways of arranging the  $N$  molecules and the  $N'$  holes is

$$\frac{(N + N')!}{N!N'} \quad (9.2)$$

so the contribution to the entropy is

$$S = k \ln \frac{(N + N')!}{N!N'} \quad (9.3)$$

It is convenient to let

$$x = N'/N \quad (9.4)$$

<sup>1</sup> This model was developed independently by J. Frenkel in 1932 (*Kinetic Theory of Liquids* [New York: Oxford University Press, 1946], p. 106), by H. Eyring (*J. Chem. Phys.*, **4**, 283 [1936]), and by S. Bresler (*Acta Physicochim.*, U.R.S.S., **10**, 491 [1939]).

Then in terms of  $x$

$$E = -\frac{1}{2}zU_0N \frac{1}{1+x} \quad (9.5)$$

$$S = Nk[(1+x) \ln(1+x) - x \ln x] \quad (9.6)$$

If we now form

$$\begin{aligned} A &= E - TS \\ &= -\frac{1}{2}zU_0N \frac{1}{1+x} - NkT[(1+x) \ln(1+x) - x \ln x] \end{aligned} \quad (9.7)$$

the system is most stable when  $A$  is a minimum. It has been customary to find this minimum by placing  $dA/dx = 0$ , which leads to the equation

$$\frac{1}{2}zU_0N \frac{1}{(1+x)^2} - NkT \ln \frac{1+x}{x} = 0 \quad (9.8)$$

which has the approximate solution

$$x = e^{-zU_0/2kT} \quad (9.9)$$

if  $zU_0/2kT \gg 1$ . According to this, the stable state is one with no holes only at  $T = 0$ . At low temperatures there is a small number of holes, and near the temperature

$$T = zU_0/2k \quad (9.10)$$

the number of holes increases very rapidly.

One might expect that this onset of hole formation is connected with the melting of the crystal, and such an interpretation has in fact been made. However, there is a difficulty in the above argument. If Equation (9.7) is plotted as a function of  $x$ , it is seen that as  $x$  increases from 0 to  $\infty$ , the value of  $A$  falls until the minimum given by (9.9) is reached. It then rises for a while, but finally goes through a maximum and then falls to  $-\infty$ . In other words, at any temperature, the value of  $A$  can be lowered by a sufficiently large increase in  $x$ . The model in its present form is, therefore, unstable.

This might have been expected, for, in the treatment given above no account of pressure has been taken, and at zero pressure any crystal is unstable: it will sublime. The effect of pressure can be included very easily. Instead of using  $A$  we should have used the free energy  $F$  formed by adding to  $A$  the product  $PV$  of the pressure and the volume. Now if  $v_0$  is the volume of the crystal per lattice site, the total volume of the crystal is

$$V = Nv_0(1+x) \quad (9.11)$$

and the free energy is

$$\begin{aligned} F &= -\frac{1}{2}NzU_0 \frac{1}{1+x} + NPv_0(1+x) \\ &\quad - NkT[(1+x) \ln(1+x) - x \ln x] \end{aligned} \quad (9.12)$$

Typical plots of  $F$  as a function of  $x$  are shown in Fig. 3. The curves now show *two* minima and the system is stable for the value of  $x$  corresponding to the lower of the two. One minimum is roughly at

$$x = e^{-(zU_0 + 2Pv_0)/2kT} \quad (9.13)$$

and the other at

$$x = kT/Pv_0 \quad (9.14)$$

The value of  $F$  at the first minimum is roughly

$$F_1 = -NzU_0 \quad (9.15)$$

and that at the second is

$$F_2 = -NkT \ln (kT/Pv_0) \quad (9.16)$$

If  $P > P_0$ , where

$$P_0 = (kT/v_0)e^{-zU_0/kT} \quad (9.17)$$

the first is the lower minimum, and if  $P < P_0$  the second is the stable position.

Our model therefore now shows two different states, with a discontinuous jump from one to the other. One state is stable at low temperatures and high pressures, the other at high temperatures and low pressures, the boundary between them on a pressure-temperature diagram being given by Equation (9.17). The low temperature-high pressure phase goes continuously to the ideal crystal as the temperature is lowered. It must, therefore, correspond

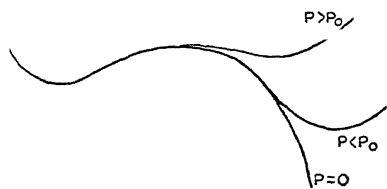


FIG. 3. Variation of Free Energy with  $x$  (Ratio of Holes to Molecules).

to the solid. The high temperature-low pressure form, on the other hand can be shown by combining Equations (9.11) and (9.14) to have the equation of state

$$V = Nv_0 \left( 1 + \frac{kT}{Pv_0} \right) \quad (9.18)$$

and, at high temperatures, this becomes the equation of state of an ideal gas. Our model still does not describe the liquid state, in the sense that it predicts both the process of fusion and that of evaporation.

However, the formation of holes in a liquid in a manner similar to the formation of holes in a solid is probably a good model for the evaporation process. What is missing in the discussion so far is a model for the melting process. If some new feature can be added to our model which will produce three minima in a plot of the free energy against the parameters of the system, the problem will at least be qualitatively solved.

(10) **Free Volume:** One possibility, developed largely by Eyring and his coworkers,<sup>1</sup> for the improvement of the hole model is to abandon the crystal lattice and to assume that each molecule of the liquid is confined in a small volume by the surrounding molecules, but that within this volume the molecule is as free to move as a molecule of an ideal gas.

This last assumption seems rather forced at first thought, for each molecule of a liquid is subject to the strong fields of its neighbors. These fields, however, are directed in all directions, and for the most part counteract each other. The extent of this cancellation has been studied carefully by Lennard-Jones and Devonshire<sup>2</sup> on the assumption of an attractive force varying as the inverse seventh power of the distance and a repulsive force varying as the inverse thirteenth power. For a molecule moving in the field of twelve neighbors they find that the potential energy is very nearly constant until the central molecule is almost in contact with one of its neighbors, when the potential energy rises very rapidly. Eyring's assumption of a constant potential energy within the "hole" occupied by each molecule is therefore not unreasonable, and certainly better than the other simple choices, such as harmonic restoring forces.

The volume which is available to the center of an average molecule in its motion is called the free volume of the molecule. This volume is not equal to the volume of the hole in which the molecule moves, for the molecule itself occupies a large fraction of the space. Nor is the free volume to be put equal to the volume of the hole minus the volume of the molecule, for the hole has narrow crevices between the molecules on its boundary into which the central atom can not squeeze. The relationship between the free volume of a liquid, the total volume, and the volume of the molecules is therefore rather complex. We shall return to this point later: for the present it is best to treat the free volume as a characteristic property of a liquid, to be evaluated experimentally.

If we now assume that the only effects of the intermolecular forces are, first, a lowering of the potential energy of the system as a whole, and second, the restriction of the free volume in which the molecules may move, we may treat the liquid in many respects as though it were an ideal gas. Now the thermodynamic properties of any system can all be expressed in terms of its partition function  $Q$ , which for an ideal gas has the form

$$Q = \left( \frac{2\pi mkT}{h^2} \right)^{3/2} VJ \quad (10.1)$$

where  $m$  is the mass of a molecule,  $k$  is Boltzmann's constant,  $T$  is the absolute temperature,  $h$  is Planck's constant,  $V$  is the volume, and  $J$  is the partition function for the internal motions of the molecule. The only modifications necessary to express the properties of our liquid molecule are first, the intro-

<sup>1</sup> H. Eyring, *J. Chem. Phys.*, **4**, 283 (1936); H. Eyring and J. Hirschfelder, *J. Phys. Chem.*, **41**, 249 (1937); J. F. Kinkaid and H. Eyring, *J. Chem. Phys.*, **5**, 587 (1937); R. F. Newton and H. Eyring, *Trans. Faraday Soc.*, **33**, 73 (1937); J. Hirschfelder, D. Stevenson, and H. Eyring, *J. Chem. Phys.*, **5**, 896 (1937).

<sup>2</sup> J. E. Lennard-Jones and A. F. Devonshire, *Proc. Roy. Soc.*, **A165**, 1 (1937).

duction of a factor  $e^{-\epsilon/kT}$ , where  $\epsilon$  is the mean potential energy of a molecule, and second, the replacement of the total volume  $V$  by the free volume  $V_f$ . Hence we shall write for a liquid

$$Q = \left( \frac{2\pi mkT}{h^2} \right)^{3/2} V_f J e^{-\epsilon/kT} \quad (10.2)$$

This partition function, however, is open to two different interpretations. One of these is to regard each molecule as permanently confined in its cell. In this case  $V_f$  is the free volume of a single cell. To distinguish this volume from the total free volume of the liquid we shall call it  $v_f$  and reserve the symbol  $V_f$  for the total free volume. If the liquid contains  $N$  molecules we then have  $V_f = Nv_f$ . In this case the proper relationship between the work function  $A$  and the partition function  $Q$  is that ordinarily used for a solid:

$$A = -NkT \ln Q \quad (10.3)$$

or

$$A = -NkT \ln \left[ \left( \frac{2\pi mkT}{h^2} \right)^{3/2} v_f J e^{-\epsilon/kT} \right] \quad (10.4)$$

On the other hand it may be assumed that there is sufficient freedom of motion of the molecules of a liquid so that in time any molecule may occupy any part of the whole free volume of the liquid. If this interpretation is adopted, the  $V_f$  in Equation (10.2) is to be taken as the total free volume. However, the relationship between the partition function and the work function is also changed in this interpretation and the appropriate equation is that for a gas

$$A = -kT \ln (Q^N/N!) \quad (10.5)$$

If we replace  $N!$  by Stirling's approximation  $(N/e)^N$ , this becomes

$$\begin{aligned} A &= -kT \ln \left[ \left( \frac{2\pi mkT}{h^2} \right)^{3/2} V_f J e^{-\epsilon/kT} e/N \right]^N \\ &= -NkT \ln \left[ \left( \frac{2\pi mkT}{h^2} \right)^{3/2} e v_f J e^{-\epsilon/kT} \right] \end{aligned} \quad (10.6)$$

If we denote the work function based on the solid-like interpretation (Equation [10.4]) by  $A_s$  and the work function based on the gas-like interpretation (Equation [10.6]) by  $A_g$ , we find

$$\begin{aligned} A_g - A_s &= -NkT \ln e \\ &= -NkT \end{aligned} \quad (10.7)$$

In terms of the entropy  $S = -\frac{\partial A}{\partial T}$

$$S_g - S_s = Nk = R \quad (10.8)$$

per mole of liquid. This difference of  $R$  in the entropy as obtained from the two interpretations is known as the communal entropy. Physically it is to be interpreted as the entropy due to the disorder which arises when the molecules become sufficiently free to exchange places with each other. It is certain that a solid at the absolute zero does not possess this entropy. It is equally certain that any gas does possess it. Therefore if a solid at the absolute zero is heated, converted into a liquid, and the liquid finally vaporized, the communal entropy must appear at some stage. It is natural to suppose that the communal entropy appears at the point at which the molecules become free to move, i.e., the melting point. Eyring assumes that the communal entropy appears entirely during the melting process, and therefore adopts Equation (10.6) for the work function of a liquid. This is probably an oversimplification, as we shall see when we discuss the fusion process, but nevertheless it is not too far from the truth.

(11) **Determination of Free Volume:** Before Equation (10.6) can be of much service it is necessary to find a method of evaluating  $v_f$ . A rough estimate can easily be obtained. Let us imagine that the molecules of the liquid are arranged in a simple cubic lattice with the lattice constant  $\delta$ . Then the total volume per molecule,  $v$ , is simply  $\delta^3$ . If we now consider all of the molecules to be fixed except one, then the chosen molecule can move in a space which is roughly cubical. Let us consider the motion of the molecule along one of the lattice edges. If the diameter of the molecules were very small compared to  $\delta$ , the molecule could move a distance  $\delta$  to either side of its original position. If, on the other hand, the diameter of a molecule is  $d$ , the distance the molecule can move to either side is  $\delta - d$ , making a total distance of  $2(\delta - d)$  in which the molecule is free to move. The volume accessible to the center of the molecule is, therefore, approximately the cube of this, or

$$v_f = 8(\delta - d)^3 \quad (11.1)$$

It has been shown by Hirschfelder, Stevenson and Eyring<sup>1</sup> that this equation holds for all types of packing in which the free volume is similar in shape to the unit cell of the lattice provided that  $d$  is defined as the cube root of the volume per molecule when the molecules are in contact.

Up to this point the molecules have been considered as rigid spheres. The lack of perfect rigidity of actual molecules will be manifested by a dependence of the free volume on temperature. Since at high temperatures the increased kinetic energy of the molecules will cause the molecules to penetrate each other's potential fields to a greater depth, the free volume should increase with temperature. To take account of this penetration, Kincaid and Eyring<sup>2</sup> have shown that Equation (11.1) should be replaced by

$$v_f = \left[ 2(\delta - d) + \left( \frac{h^2}{2\pi mkT} \right)^{1/2} \frac{T}{\theta_i} \right]^3 \quad (11.2)$$

<sup>1</sup> *J. Chem. Phys.*, **5**, 896 (1937).

<sup>2</sup> *Ibid.*, **5**, 587 (1937).



where  $\theta_i$  is a characteristic temperature for each liquid, which is closely related to the Debye temperature for the solid.

(12) **Fusion:** The melting of a crystal is a typical example of a process in which a system is faced with a choice between two states, one of which is characterized by a low energy and a high degree of order, the other by a higher energy and a smaller degree of order. At low temperatures the solid is stabilized by its low energy, while at high temperatures the high disorder, and therefore entropy, of the liquid causes the solid to melt. The melting point is therefore the temperature,  $T_f$ , at which the latent heat of fusion,  $\Delta H_f$ , is exactly equal to  $T_f \Delta S_f$ , where  $\Delta S_f$  is the increase in entropy.

The latent heat of fusion is essentially the work which must be done to overcome the attractive forces between the molecules during the change from crystal to liquid. As we have already seen, the mean intermolecular distance in the liquid is always greater than that in the solid, even though the liquid may have the greater density. It is obvious, therefore, that the latent heat of fusion will be greatest for those substances having the greatest intermolecular attractions. In Table I are given the latent heats of fusion of a number of typical substances. From this table we see that the substances with the lowest heats of fusion are those which form molecular crystals, held together only by van der Waals' forces. Next come the metals, and then the salts with their strong electrostatic binding. Although no data seem to be available, the covalent crystals, such as diamond and carborundum, should have the highest heats of fusion of all.

It should be noted, however, that it is not the total bond strength between molecules which determines the heat of fusion so much as the shape of the potential energy curve in the neighborhood of the minimum. This is due to the fact that the bonds are not completely broken in the fusion process but merely stretched. It would therefore seem better to compare the hardness of the crystal with the heat of fusion than to compare the heat of fusion with the total binding energy of the crystal, but unfortunately for the possibility of deciding the question, the force constants of the bonds parallel the bond strengths too closely to permit a decision at present. In spite of this argument, it is interesting to compare the heats of fusion of these substances with their heats of vaporization. Since the heat of vaporization is essentially equal to the total strength of the bonds in the crystal, we should expect that the heat of fusion would be a rather small fraction of the heat of vaporization. This is seen to be actually the case. It has been pointed out by Slater<sup>1</sup> that the ratio of the heat of fusion to the heat of vaporization is fairly constant for substances with the same type of intermolecular binding. For molecular crystals this ratio is approximately 1/10, while for metals and for salts it is roughly 1/30. This comparison is shown in the second and third columns of Table I.

The variation in the entropy of fusion is much less than that shown by the heat of fusion. In fact an inspection of Table I shows that for monatomic

<sup>1</sup> J. C. Slater, *Introduction to Chemical Physics* (New York: McGraw-Hill Book Co., Inc., 1939), p. 260.

TABLE I  
FUSION CHARACTERISTICS OF TYPICAL SUBSTANCES \*

	$L_m$ , kg-cal/mole	$L_r$	$\frac{L_m}{L_r}$	$T_m$ , °K	$\Delta S_m$ , cal/deg
<i>Metals:</i>					
Na.....	0.63	26.2	0.024	371	1.70
Mg.....	1.16	34.4	0.034	923	1.26
Al.....	2.55	67.6	0.038	932	2.73
K.....	0.58	21.9	0.026	336	1.72
Cr.....	3.93	89.4	0.044	1823	2.15
Mn.....	3.45	69.7	0.050	1493	2.31
Fe.....	3.56	96.5	0.037	1802	1.97
Co.....	3.66	—	—	1763	2.08
Ni.....	4.20	98.1	0.043	1725	2.44
Cu.....	3.11	81.7	0.038	1357	2.29
Zn.....	1.60	31.4	0.051	692	2.32
Ga.....	1.34	—	—	303	4.42
Se.....	1.22	—	—	490	2.49
Rb.....	0.53	20.6	0.026	312	1.70
Ag.....	2.70	69.4	0.039	1234	2.19
Cd.....	1.46	27.0	0.054	594	2.46
In.....	0.78	—	—	429	1.82
Sn.....	1.72	68.0	0.025	505	3.40
Sb.....	4.77	54.4	0.088	903	5.29
Cs.....	0.50	18.7	0.027	302	1.66
Pt.....	5.33	125.	0.043	2028	2.63
Au.....	3.03	90.7	0.033	1336	2.27
Hg.....	0.58	15.5	0.037	234	2.48
Tl.....	0.76	43.0	0.018	576	1.32
Pb.....	1.22	46.7	0.026	601	2.03
Bi.....	2.51	47.8	0.053	544	4.61
<i>Ionic substances:</i>					
NaF.....	7.81	213	0.037	1265	6.19
NaCl.....	7.22	183	0.039	1073	6.72
KF.....	6.28	190	0.033	1133	5.53
KCl.....	6.41	165	0.039	1043	6.15
KBr.....	2.84	159	0.018	611	4.65
AgCl.....	3.15	—	—	728	4.33
AgBr.....	2.18	—	—	703	3.10
TiCl.....	4.26	—	—	700	6.09
TlBr.....	5.99	—	—	733	8.18
LiNO <sub>3</sub> .....	6.06	—	—	523	11.6
NaNO <sub>3</sub> .....	3.76	—	—	583	6.45
KNO <sub>3</sub> .....	2.57	—	—	581	4.42
AgNO <sub>3</sub> .....	2.76	—	—	481	5.72
NaClO <sub>3</sub> .....	5.29	—	—	528	9.90
NaOH.....	1.60	—	—	591	2.71

\* J. C. Slater, *Introduction to Chemical Physics* (New York: McGraw-Hill Book Co., Inc., 1939), p. 259.

TABLE I (Continued)

	$L_m$ , kg-cal. mole	$L_r$	$\frac{L_m}{L_r}$	$T_m$ , °K	$\Delta S_m$ , cal/deg
<i>Ionic substances: cont.</i>					
KOH.....	1.61	—	—	633	2.54
K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> .....	8.77	—	—	671	13.07
BaCl <sub>2</sub> .....	5.75	—	—	1232	4.65
CaCl <sub>2</sub> .....	6.03	—	—	1047	5.77
PbCl <sub>2</sub> .....	5.65	—	—	771	7.32
PbBr <sub>2</sub> .....	4.29	—	—	761	5.63
PbI <sub>2</sub> .....	5.18	—	—	648	8.00
HgBr <sub>2</sub> .....	4.62	—	—	508	9.09
HgI <sub>2</sub> .....	4.50	—	—	523	8.60
<i>Molecular substances:</i>					
H <sub>2</sub> .....	0.028	0.22	0.13	14	2.0
NO.....	0.551	3.82	0.14	110	5.02
H <sub>2</sub> O.....	1.43	11.3	0.13	273	5.25
O <sub>2</sub> .....	0.096	2.08	0.05	54	1.78
A.....	0.280	1.88	0.15	83	3.38
NH <sub>3</sub> .....	1.84	7.14	0.26	198	9.30
N <sub>2</sub> .....	0.218	1.69	0.13	63	3.46
CO.....	0.200	1.90	0.11	68	2.94
HCl.....	0.506	4.85	0.10	159	3.20
CO <sub>2</sub> .....	1.99	6.44	0.31	217	9.16
CH <sub>4</sub> .....	0.224	2.33	0.10	90	2.49
HBr.....	0.620	5.79	0.11	187	3.31
Cl <sub>2</sub> .....	1.63	7.43	0.22	170	9.59
CCl <sub>4</sub> .....	0.577	8.0	0.07	250	2.30
CH <sub>3</sub> OH.....	0.525	9.2	0.06	176	2.98
C <sub>2</sub> H <sub>5</sub> OH.....	1.10	10.4	0.11	156	7.10
CH <sub>3</sub> COOH.....	2.64	20.3	0.13	290	9.21
C <sub>6</sub> H <sub>6</sub> .....	2.35	8.3	0.28	278	8.45

substances the entropy of fusion is always of the magnitude of 2 cal/deg. For the simple binary salts we find that the same value also holds if we reckon the entropy of fusion per ion, rather than per molecule. For more complicated substances, however, the entropy of fusion is consistently higher than this value. To account for the entropy of fusion we have three principal sources. First, because of the increased volume of the liquid, the molecules have more room in which to move. This will give rise to an increase in entropy similar to that experienced by an ideal gas in an isothermal expansion. Second, we have the communal entropy, already discussed. Third, we have the entropy which arises if one or more degrees of freedom of the molecule have been hindered by the neighboring molecules in the crystal, but are freed in the transition to the liquid. For example, a molecule in the free state may have free rotation about one of its bonds, while in the crystal the surrounding molecules may hinder the rotation to such an extent that it is reduced to a rotatory

vibration. If the liquid is sufficiently loose in its structure so that this rotation is possible in the liquid, the increased freedom of motion will appear as an additional entropy of fusion.

The increase in entropy caused directly by the increase in volume is small. If we estimate it crudely by using the formula for the entropy of expansion of an ideal gas

$$\Delta S = R \ln (V_2/V_1) \quad (12.1)$$

then an increase in entropy of  $R$  would require the volume of the liquid to be 2.7 times that of the solid, whereas the usual expansion is seldom more than 10 per cent. Since the actual expansion is relatively so small, we may expand the logarithm in Equation (12.1), and write

$$\Delta S \approx R \Delta V/V \quad (12.2)$$

From this it is apparent that the volume increase should contribute only a few tenths of a calorie per degree to the entropy of fusion. It should be noted, however, that, strictly speaking, the free volume rather than the total volume should be used in Equation (12.1). If this is done the contribution may be much larger, for the free volume of the solid is quite small.

The effect of the volume change on the entropy of fusion can be taken into account more exactly by using Equation (10.6) for the work function of the liquid and the approximate expression

$$A = -NkT \ln \left( \frac{T}{\theta_s} \right)^3 e^{-E'/kT} \quad (12.3)$$

for the solid. In this equation  $\theta_s$  is the characteristic temperature of the solid and  $E'$  is the binding energy per molecule. Treating these expressions in the ordinary way, we find for the entropy of fusion

$$\begin{aligned} -\frac{1}{2}R + 3R \ln \left[ \frac{\theta_s}{\theta_l} + 2 \left( \frac{2\pi mk}{h^2 T} \right) \theta_s (\delta - d) \right] \\ + 3RT \left[ \frac{1 + \frac{1}{2} \left( \frac{2\pi mkT}{h^2} \right)^{1/2} \theta_l (\alpha_l \delta - \alpha_s d)}{2T + 4 \left( \frac{2\pi mkT}{h^2} \right)^{1/2} \theta_l (\delta - d)} \right] \end{aligned} \quad (12.4)$$

In this equation we have used Equation (11.2) for the free volume, and  $\alpha_l$  and  $\alpha_s$  are the coefficients of expansion of the liquid and solid, respectively. Ordinarily the last term in Equation (12.4) can be neglected.

In order to use this equation Hirschfelder, Stevenson and Eyring have assumed that  $\delta$  and  $d$  can be approximated by the cube roots of the molecular volumes of the liquid and the solid, while for  $\theta_l$  they find that the assumption  $\theta_l = 1.1\theta_s$  gives good agreement. The entropies of fusion obtained from

Equation (12.4) are compared with experiment in Table II. Since the "internal" entropy of fusion has been neglected, the theory can be applied directly only to monatomic substances. It is evident from Table II that the agreement with experiment is very good.

TABLE II \*

Substance	$T_f$	$\theta_i$	$V_l$	$V_s$	$\Delta S_f^\dagger$ (calc.)	$\Delta S_f^\ddagger$ (calc.)	$\Delta S_f$ (exp.)
A.....	84	85	28.0	25.1	3.24	2.78	3.32
Hg.....	234	84	14.7	14.2	2.89	2.42	2.38
Pb.....	600	88	19.5	18.8	2.63	2.12	2.17
Na.....	371	172	24.8	24.2	2.43	1.90	1.70
K.....	337	100	47.0	45.9	2.38	1.85	1.70
Cs.....	299	42	72.3	70.4	2.41	1.88	1.67
Cu.....	1356	315	8.00	7.60	2.91	2.43	2.36
Ag.....	1234	215	11.5	11.1	2.68	2.18	2.19
Au.....	1336	170	11.45	10.9	2.95	2.48	2.34

\* J. Hirschfelder, D. Stevenson, and H. Eyring, *J. Chem. Phys.*, 5, 899 (1937).

$\dagger \theta_l = \theta_s$ .

$\ddagger \theta_l = 1.1 \theta_s$ .

For polyatomic molecules the entropy of Equation (12.4) is only part of the total entropy of fusion. In some simple cases the entropy due to the freeing of frozen-in degrees of freedom can be estimated. For example, the entropy of fusion of a number of linear molecules has been calculated by Hirschfelder, Stevenson and Eyring on the assumption that the molecules are free to rotate in the liquid but can only librate in the solid. Assuming a frequency of libration of  $50 \text{ cm}^{-1}$ , and using the known moments of inertia of the molecules, the entropy of libration,  $S_{\text{lib}}$ , and the entropy of rotation,  $S_{\text{rot}}$ , can be calculated.

TABLE III \*

Substance	$T_f, ^\circ\text{K}$	$S_{\text{rot}}$	$S_{\text{lib}}$	$\Delta S_f$ (calc.)	$\Delta S_f$ (exp.)
Cl <sub>2</sub> .....	238.4	13.60	8.75	6.84	6.77
Br <sub>2</sub> .....	266	16.05	9.91	8.85	9.51
I <sub>2</sub> .....	386.5	18.30	10.70	9.59	9.45
CS <sub>2</sub> .....	161.1	14.50	7.20	9.29	8.37
N <sub>2</sub> O.....	182.3	13.40	7.70	7.69	8.58

\* J. Hirschfelder, D. Stevenson, and H. Eyring, *J. Chem. Phys.*, 5, 901 (1937).

If we neglect the entropy of volume increase, the entropy of fusion should be simply  $S_{\text{rot}} - S_{\text{lib}} + R$ , the last term being the communal entropy. The results, shown in Table III, are in fair agreement with experiment.

It will be noticed in Table III that the entropy of fusion of all these substances is approximately the same. In general we might expect that the en-

tries of similar substances should always be approximately equal. In many cases, however, this rule is disguised by the fact that there may be a transition below the melting point in which one or more degrees of freedom become active. If in a series of similar compounds some have this transition below the melting point, and some at the melting point, then the entropy of the transition is included in the entropy of fusion for some of the compounds and not for the others. In such cases Eyring has pointed out that the sum of the entropy of fusion and the entropy of transition, rather than the entropy of fusion alone, should be constant for the series.

If entropies of fusion varied as widely as do heats of fusion, there would be little parallelism between heats of fusion and melting points. Since, however, the actual range of values of entropies of fusion is small, there is a rough proportionality between melting point and heat of fusion. It is this which is behind our intuitive feeling that a weakly bound crystal, such as solid argon, should have a low melting point, while a strongly bound crystal, such as sodium chloride, should have a high melting point. The fact that all entropies of fusion are not exactly equal, but vary from about 1.5 cal/deg to 10 cal/deg, introduces some complication. For example, magnesium has a heat of fusion of 1,160 cal and ethyl alcohol has a heat of fusion of 1,100 cal. From the closeness of these values we might expect that their melting points would be at least approximately equal. The actual melting points, however, are 923°K and 156°K. An inspection of the entropies of fusion immediately reveals the discrepancy. For magnesium the entropy of fusion is 1.26 cal/deg, nearly the normal value  $R$  for a monatomic substance. For ethyl alcohol, on the other hand, the entropy of fusion is 7.10 cal/deg. The high value of course indicates that some new degrees of freedom (which were frozen-in in the solid) are active in the liquid. These degrees of freedom are probably the rotations of the molecule as a whole and the internal rotations about the C—C bond. The tendency of these rotations to break loose produces an added tendency for the crystal to melt. The melting point of ethyl alcohol is therefore much lower than one would expect. The same result can be explained in another way by considering the freezing process. In liquid magnesium the atoms are practically spheres and are not far from having the same packing as the solid. Therefore the amount of order which must be created in order to solidify the liquid is small and the freezing process can take place easily, i.e., at a high temperature. In alcohol, on the other hand, the molecules are more complex, and are irregularly arranged in the liquid. To bring these molecules into the perfect order required by the crystal is far more difficult and the entropy of fusion much higher. We therefore conclude again that ethyl alcohol will freeze at a much lower temperature than will magnesium.

(13) **Fusion as an Order-Disorder Transition:** The simple theory of melting which we have been discussing is deficient in several respects. The principal difficulty is that it gives no explanation of the change in volume on melting, but regards this volume change as an arbitrary parameter. A complete theory, on the other hand, would predict the volume change as well as the heat and

entropy of fusion. As yet no exact theory has been constructed to do this, but there has been a promising start in this direction by Lennard-Jones and Devonshire.<sup>1</sup>

These authors picture a solid as an alloy of atoms and holes, the atoms at low temperature occupying all the sites of a perfect lattice while the holes occupy all the sites of a second perfect lattice interpenetrating the first. The situation is analogous to the arrangement of checkers on a checker-board, the pieces (atoms) occupying the black squares and the holes the white squares. The lattice sites which in the solid are occupied by atoms are called  $\alpha$ -sites; those which are occupied by holes,  $\beta$ -sites. The arrangement of atoms and holes is shown in Fig. 4a.

If we now imagine an atom moved from an  $\alpha$ -site to a  $\beta$ -site, it finds itself at a shorter distance from some of its neighbors than before, and at a longer distance from the others. Thus some of the bonds holding the lattice together are compressed, while others are stretched. This will have the effect of increasing the energy of the system. If this increase in energy is  $W$  for each pair of close neighbors thus formed, the increase in energy will be  $mW$ , where  $m$  is the number of close neighbors to the new site for our atom.

If  $W$  were zero, so that each atom could change freely from  $\alpha$ -site to  $\beta$ -site, or vice-versa, the atoms and holes would be arranged at random on the two lattices, with an equal number of atoms on each. The randomness of this distribution leads to an increased entropy over the original ordered arrangement. The natural tendency of the entropy to increase therefore tends to break up the ordered arrangement of the solid, and produce a disordered arrangement.

The entropy of disorder considered here is closely allied to the communal entropy, since both correspond to an increase in the freedom of motion of the molecules. For complete randomness the entropy is simply the entropy of mixing of the atoms and the holes, and has the value  $R \ln 2$  or approximately  $0.69R$ . The difference between this and the value  $R$  given to the communal entropy arises from the fact that in the present theory the atoms are confined to the two lattices of  $\alpha$ - and  $\beta$ -sites. If this restriction were removed, the entropy would increase still further and would presumably approach the value  $R$ .

In an actual system the interatomic forces tend to produce the ordered arrangement of the solid, while the entropy tends to produce a disordered arrangement. There are, however, two distinct types of order, generally known as long-range and short-range order. The long-range order is determined simply by the fraction  $q$  of the atoms which occupy  $\alpha$ -sites. If the order is perfect, this fraction is 1, while for complete disorder it is  $\frac{1}{2}$ . The degree of long-range order,  $\Sigma$ , is defined as  $2q - 1$ , so that for perfect order, when  $q = 1$ ,  $\Sigma = 1$ , and for a random distribution, when  $q = \frac{1}{2}$ ,  $\Sigma = 0$ . Suppose, however, that we split a perfectly ordered arrangement into two equal parts, and

<sup>1</sup> J. E. Lennard-Jones and A. F. Devonshire, *Proc. Roy. Soc.*, **A163**, 53 (1937); **A165**, 1 (1937); **A169**, 317 (1939).

then bodily move one half from the  $\alpha$ -lattice to the  $\beta$ -lattice. The value of  $q$  is now  $\frac{1}{2}$  so that  $\Sigma = 0$ . In spite of the disappearance of long-range order, there is still perfect order in the neighborhood of all of the atoms except those near the boundary between the two pieces, so that we might say that the short-range order is still nearly perfect. To arrive at a measure of the short-range

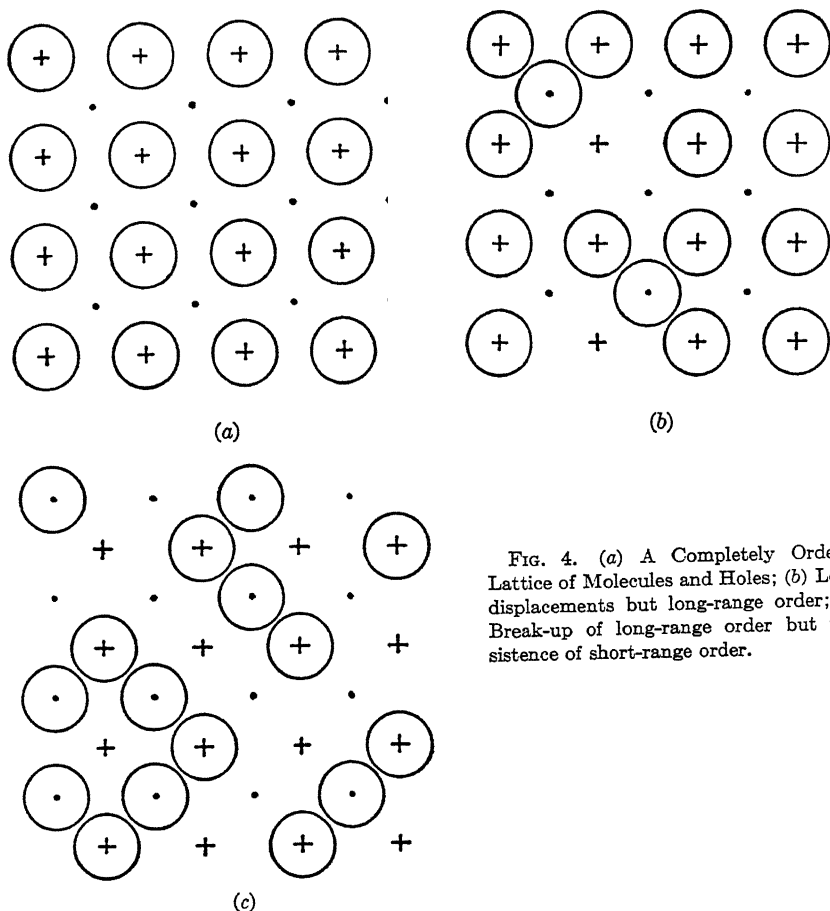


FIG. 4. (a) A Completely Ordered Lattice of Molecules and Holes; (b) Local displacements but long-range order; (c) Break-up of long-range order but persistence of short-range order.

order, we consider each atom individually. In a state of perfect order each atom is surrounded by a set of lattice points which are occupied only by holes. As the order decreases, these points may become occupied by atoms. We may, therefore, take as a measure of the short-range order the average fraction,  $r$ , of closely neighboring lattice points which are occupied by holes. This fraction will be 1 in perfect order, and  $\frac{1}{2}$  in complete disorder. The degree of short range order,  $\sigma$ , is defined by  $\sigma = 2r - 1$ , and again is 1 for perfect order



and 0 for complete disorder. It will be noticed that in our example of a system with short-range order, but not long-range order, that  $\sigma$  will be nearly 1 if the two half lattices are equal.

In Figs. 4b and 4c are shown two typical states with partial disorder. In Fig. 4b the fraction of  $\alpha$ -sites occupied by atoms is  $\frac{1}{2}$  so that  $\Sigma = 0.75$ . The short-range order  $\sigma$  in the same figure is found to be 0.625 which is of the same order of magnitude as the long-range order. In Fig. 3c  $\Sigma = 0$ , but  $\sigma$  is easily

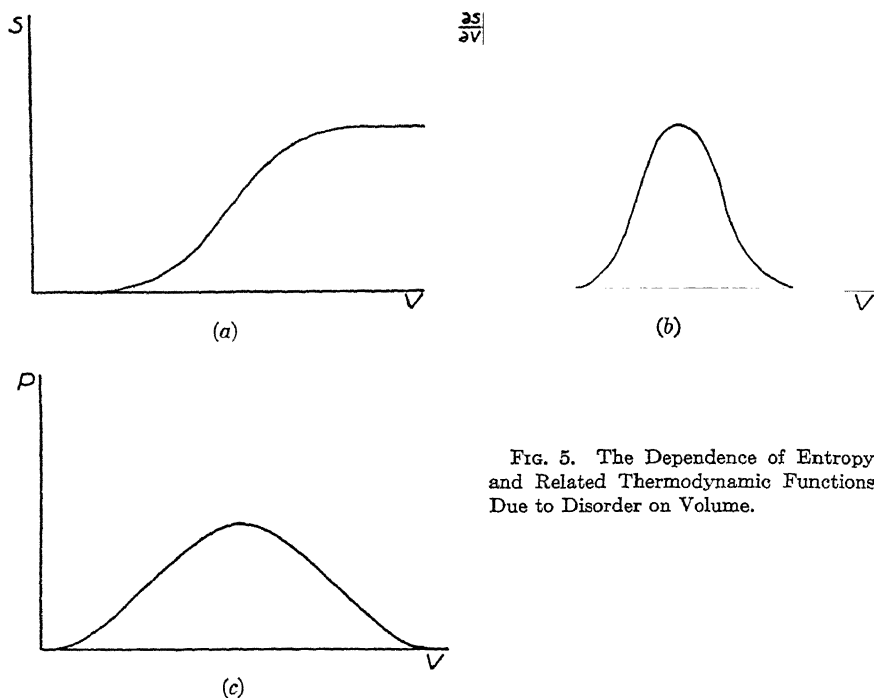


FIG. 5. The Dependence of Entropy and Related Thermodynamic Functions Due to Disorder on Volume.

seen to be 0.3125, so that there remains short-range order even after the long range order has disappeared.

If we now consider the entire lattice system to be expanded, the ordering interatomic forces will be weakened, and the system will, therefore, tend to a more disordered state. From what we have already seen, the long-range order will disappear first, and then the short-range order. The disappearance of the long-range order, however, is essentially a symptom of the passage from the solid to the liquid state, for we have already seen that although a liquid has no regular crystal form, i.e., no long-range order, the atoms surrounding a given atom are for the most part in a regular arrangement, i.e., there is still short-range order. We shall therefore define the process of fusion as the process of losing long-range order.

This definition seems at first to imply that melting is a gradual process, but a closer examination shows that this is not the case. This can most easily be seen by considering the pressure, which can be derived from the entropy by the integration of the thermodynamic relationship  $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ . As the long-range order disappears on increasing the volume, the entropy of disorder rises from zero to a constant positive value. The behavior of this part of the entropy as a function of volume is shown in Fig. 5a. The derivative  $\left(\frac{\partial S}{\partial V}\right)_T$  or  $\left(\frac{\partial P}{\partial T}\right)_V$  is shown in Fig. 5b, and the pressure in Fig. 5c. This "disorder pressure" can be crudely visualized by an analogy due to Lennard-Jones. A certain number of oranges, packed in a regular arrangement, will just fill a crate. If the oranges are removed from the crate and then put back again in a haphazard fashion, it will now require considerable pressure to put the lid back on the crate. This pressure is the disorder pressure. If the crate is made larger the disorder pressure falls to zero. If the crate is made smaller the pressure becomes so great that the oranges are forced into a regular arrangement. While the pressure may still be large it is no longer due to disorder, so that the disorder pressure again falls to zero at low volumes.

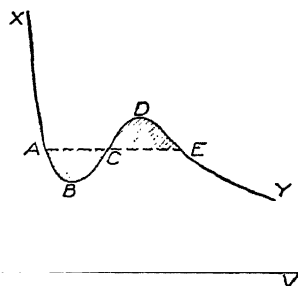


FIG. 6.  $P$ - $V$  Isotherm in the Neighborhood of the Melting Point.

To this disorder pressure there must be added the ordinary pressure due to the kinetic energy of the molecules and the repulsions between them. In general the ordinary pressure decreases with increasing volume, but not fast enough to overcome the sudden rise in the disorder pressure, so that at the point where long-range order disappears the total pressure rises as the volume increases, as shown in Fig. 6. This situation is obviously unstable, and separation into two phases will occur. The specific volumes of these phases are determined by Maxwell's law of equal areas, i.e., that the horizontal line  $ACE$  should make the area  $ABC$  equal to the area  $CDE$ . The difference in free energy between the states represented by the points  $A$  and  $E$  is then zero, and the states are in equilibrium. All the states between  $A$  and  $E$  are therefore unstable. If we now consider an isothermal expansion process, beginning with a highly compressed solid at the point  $X$  in Fig. 6, the pressure will fall rapidly as we pass along the curve  $XA$ . At  $A$ , however, a further increase in volume causes the appearance of liquid at the point  $E$ , and the solid continues to melt until nothing but liquid remains. Further expansion will then cause the pressure to fall again, along the curve  $EY$ .

The pressure-volume curve given in Fig. 6 is very similar to that first suggested by van der Waals for the transition from the liquid state to the gas. This similarity suggests that at sufficiently high temperatures the maximum and minimum may coalesce, and that above some critical temperature the distinction between solid and liquid may disappear. As yet, however, the theory of melting is not sufficiently advanced to decide this point, but it is probable that if a critical point exists for the melting process, it occurs at far higher pressures than have yet been attained.

The mathematical details of Lennard-Jones and Devonshire's theory are too complex to be discussed here. It should be noted, however, that their theory contains only one adjustable parameter. If this is chosen in such a way that the melting point of the solid is correct, then the heat and entropy of fusion are determined, and also the change in volume. From the same calculation the coefficient of expansion may also be found, so that there are three independent checks on the theory. (The heat of fusion, being determined by the entropy of fusion and the melting point, is not independent.) The calculations have been carried out for argon and nitrogen, and the comparison with experiment is shown in Table IV. The agreement is remarkably good, and is strong evidence in favor of this theory of melting.

TABLE IV

	Melting point, °K	$\Delta V$ , %		$\Delta S$ , cal/deg		Coefficient of expansion	
		Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
Ar.....	83.8	13	12	3.45	3.35	0.0049	0.0045
N <sub>2</sub> .....	63.2	8	9	2.58	2.73	0.0048	0.0059

(14) **Evaporation and Condensation:** In many respects the evaporation of a liquid resembles the melting of a solid. Both processes are always accompanied by an increase in both the heat content and the entropy, and also by a change in specific volume. In the case of evaporation, however, these effects are much larger than they are for fusion. In particular the volume change, which is sometimes negative in fusion, is always positive in evaporation; and instead of being of the order of 10 per cent, it is now usually about 100 times the volume of the liquid.

During the enormous increase in volume, the molecules are pulled apart from their neighbors against the attractive forces which hold the liquid together. The heat of evaporation is essentially the energy necessary to overcome these forces, and is therefore necessarily greater than the heat of fusion, which represents the energy necessary to cause only a rather small increase in the mean intermolecular distance. Like the heat of fusion, the heat of evaporation depends principally on the type of force holding the molecules together. It is least for such molecules as those of the "permanent" gases, which are held

together only by van der Waals' forces, and greatest for salts and covalently bound molecules.

It has long been recognized, however, that the entropy of vaporization of different liquids is always of the same order of magnitude. One of the earliest studies was made by Trouton<sup>1</sup> who enunciated the famous rule that the quotient of the heat of vaporization by the absolute temperature of the boiling point is the same for all liquids. In other words, the entropy of vaporization is constant. A glance at the entropies of vaporization (for  $p = 1$  atm) given in Table V shows, however, that Trouton's rule applies only roughly, and departs seriously from the truth if the boiling points are low.

TABLE V  
BOILING POINTS, LATENT HEATS OF VAPORIZATION AND ENTROPIES OF  
VAPORIZATION OF SOME TYPICAL LIQUIDS

Molecule	P., °K	$\Delta H$ , cal	$\Delta S$ , cal/deg ( $p = 1$ atm)	$\Delta S$ , cal/deg ( $v = 22.4$ l)
Nitrogen.....	79	1,400	17.8	22.5
Oxygen.....	97	1,800	18.6	22.5
Chlorine.....	235	5,360	22.8	22.7
Pentane.....	307	6,810	22.2	21.9
Isopentane.....	307	7,000	22.8	22.3
Hexane.....	341	7,630	22.4	22.1
Carbon tetrachloride	347	7,840	22.6	21.9
Benzene.....	351	8,140	23.2	22.3
Fluorobenzene.....	356	8,260	23.2	22.3
Stannic chloride.....	385	8,860	23.0	22.1
Octane.....	396	9,350	23.6	22.5
Bromonaphthalene..	551	13,200	24.0	22.5
Mercury.....	627	14,300	22.8	21.1
Cadmium.....	937	23,800	25.4	21.3
Zinc.....	1,188	30,900	26.0	21.3

A number of modifications of Trouton's rule have been advanced to take into account the upward trend of the entropy of vaporization with the boiling point. The most successful of these is that of Hildebrand.<sup>2</sup> Hildebrand's modification consists in taking not the entropy of vaporization for a fixed pressure, (one atmosphere in the case of Trouton's rule), but rather for a fixed volume. The values in the last column of Table V are the entropies calculated for that temperature at which the molar volume of the saturated vapor has the value 22.4 l, so that for a liquid boiling at 0°C, the two entropies of vaporization would be equal. It will be noticed immediately that the upward drift of the Trouton entropy is eliminated in the Hildebrand entropy. The liquids in

<sup>1</sup> F. Trouton, *Phil. Mag.* (5), 18, 54 (1884).

<sup>2</sup> J. H. Hildebrand, *Solubility* (2d ed.; New York: Reinhold Publishing Corporation, 1936), p. 102; *J. Am. Chem. Soc.*, 37, 970 (1915); 40, 45 (1918).

Table V are all "normal" liquids. If the Hildebrand entropy is calculated for "associated" liquids the results are higher. Ammonia, water and ethyl alcohol, for example, give Hildebrand entropies of 27.2, 26.8 and 28.2 cal/deg. It is, therefore, necessary to be careful, in using the Hildebrand rule, to compare only liquids of similar structure.

Over a range of temperatures sufficiently small that the heat of vaporization of a liquid may be regarded as constant, the Clapeyron-Clausius equation may be integrated to the form

$$\ln p/p_0 = \frac{\Delta H}{R} \left( \frac{1}{T_0} - \frac{1}{T} \right) \quad (14.1)$$

If  $T_0$  is taken to be the boiling point,  $T_b$ , so that  $p_0$  is 1 atm, this becomes

$$\ln p = \frac{\Delta H}{RT_b} \left( 1 - \frac{T_b}{T} \right) \quad (14.2)$$

or

$$\ln p = \frac{\Delta S}{R} \left( 1 - \frac{T_b}{T} \right) \quad (14.3)$$

where  $\Delta S$  is the Trouton entropy. Trouton's rule can therefore be used to express the vapor pressure as a function of the temperature if the boiling point is known, or to find the boiling point if the vapor pressure is known at a single temperature. The value 23 cal/deg is a sufficiently good approximation to the Trouton entropy for most substances which are normal liquids at room temperature.

If we take as  $T_0$  the temperature at which the molar volume of the saturated vapor is 22.4 l, then (if we assume the vapor to be ideal)

$$p_0 = \frac{RT_0}{22.4} = \frac{T_0}{273} \text{ atm} \quad (14.4)$$

and the Clapeyron-Clausius equation takes the form

$$\ln p = \ln \frac{T_0}{273} + \frac{\Delta S}{R} \left( 1 - \frac{T_0}{T} \right) \quad (14.5)$$

where  $\Delta S$  is now the Hildebrand entropy. For normal liquids the value 22.1 is a good approximation for  $\Delta S$ , so that we may write Equation (14.5) in the form

$$\log p = \log T_0 + 2.40 - 4.83 \frac{T_0}{T} \quad (14.6)$$

if  $p$  is in atmospheres, or

$$\log p = \log T_0 + 5.25 - 4.83 \frac{T_0}{T} \quad (14.7)$$

if  $p$  is in millimeters of mercury. This equation again gives the complete vapor pressure curve if the vapor pressure is known at a single temperature; but,

although it is more accurate than (14.5), it is less easy to use because of the fact that a transcendental equation must be solved to find  $T_0$ . The labor of solving this equation can be lightened in some cases by using Table VI, which gives the values of  $T_b$  corresponding to a number of values of  $T_0$ .

TABLE VI

VALUES OF THE HILDEBRAND TEMPERATURE FOR DIFFERENT BOILING POINTS

$T_b$	100	200	300	400	500	600	700	800	900	1,000
$T_0$	90	194	303	416	530	647	765	886	1,006	1,128

The fact that Hildebrand's rule holds for such a large number of liquids is a strong indication that the entropy of vaporization arises from the same source for the whole series. It is obvious that the heat of vaporization has little effect on the entropy of vaporization, so that the strength of the forces holding together the molecules of the liquid is not a determining factor. Moreover, the entropy is practically the same for monatomic liquids and complex organic liquids, so that internal molecular structure can hardly be responsible. There remains only the enormous change in volume which accompanies vaporization. If we make the simple assumption that the molecules of a liquid are free to move in a free volume  $V_f$ , and in the gas in a volume  $V_g$ , and if we further assume that the whole of the entropy of vaporization is due to the volume change, then it follows that

$$\Delta S = R \ln \frac{V_g}{V_f} \quad (14.8)$$

If we add the further assumption that  $V_f$  is the same for all liquids, Hildebrand's rule is a direct consequence of our hypotheses. If we take the value 22.1 cal/deg for the Hildebrand entropy when  $V_g$  has the value 22.4 l, this equation gives for the free volume the value 0.33 cc/mole, which is certainly of the correct order of magnitude.

In the case of associated liquids it is not difficult to find the source of the additional entropy of vaporization. The liquids which are commonly considered to be associated are just those, such as water, ammonia, and the alcohols, in which hydrogen bonds between the molecules are possible. The effect of such bonds is to produce a sort of polymerization of the molecules, so that the molecules are less free to rotate in the liquid than they are in the vapor. As the liquid vaporizes, the freeing of these rotations leads to an additional entropy increase beyond that due to the volume change. This in turn leads to a boiling point which is lower than would otherwise be expected. It should be noted that hydrogen-bond formation is not essential to the formation of an associated liquid, for any force which hindered molecular rotation would have a similar effect. Nevertheless, there are few examples of associated liquids in which the associating force can not be attributed to the formation of hydrogen bonds.

(15) **The Liquid as an Imperfect Gas:** The ideas we have developed up to this point have treated the liquid as an imperfect solid. The older theories of the liquid state, on the other hand, treated the liquid as an imperfect gas. The fact that a liquid can be converted reversibly into a gas, without passing at any time through a region in which two phases are present, by simply heating the liquid under pressure to a temperature above its critical point and then allowing it to expand, is a cogent reason for believing that the liquid is somehow gas-like in structure. It seems difficult to reconcile such widely different models of liquid structure; and, as a matter of fact, the reconciliation has been made only by modifying the theory of imperfect gases in a direction which gives even the gaseous state a resemblance to the solid.

The mathematical methods of treating imperfect gases in the neighborhood of condensation are too complex to be given here, so that only a semi-quantitative treatment will be given. The method of attack is essentially that of Mayer,<sup>1</sup> to whose papers the reader is referred for rigorous detail.

Let us consider a system of  $N$  molecules confined in a volume  $V$ . If there were no forces between the molecules, the system would behave as an ideal gas. In particular, there is a definite probability of finding a group of  $j$  molecules, where  $j$  is any integer up to  $N$ , in any volume element we may select. Suppose, therefore, that we select a volume  $v_0$ , small compared to  $V$ , but large compared to the volume of a molecule, and define a "cluster" of  $j$  molecules as any group of  $j$  molecules which can be enclosed in a sphere of volume  $v_0$ . As long as the molecules are distributed at random the number  $n_j^0$  of clusters of  $j$  molecules is easily found from the laws of probability to be

$$n_j^0 = \frac{N^j v_0^{j-1}}{j! V^{j-1}} e^{-Nv_0/V} \quad (15.1)$$

Under the influence of molecular forces, however, the number of clusters of a given size will differ from that given by Equation (15.1). There are three different effects to be noticed. First of all, the repulsive forces which act between all real molecules prevent pairs of molecules from approaching too closely. These forces, therefore, have the effect of decreasing the number of clusters of more than one molecule. The number of "clusters of one molecule," however, i.e., the number of isolated molecules with no neighboring molecules within a volume  $v_0$ , will be increased. The attractive forces act in the opposite way, tending to increase the number of clusters of more than one molecule, and decrease the number of clusters of one molecule. The third effect is that of temperature. The Boltzmann distribution law expresses the tendency of molecules to occupy higher energy levels at high temperatures. Since the repulsive forces increase the energy, they are most important for molecules with high energies, and therefore for high temperatures. The attractive forces, on the

<sup>1</sup> J. E. Mayer, *J. Chem. Phys.*, 5, 67 (1937); J. E. Mayer and P. G. Ackermann, *ibid.*, 5, 74 (1937); J. E. Mayer and S. F. Harrison, *ibid.*, 6, 87 (1938); 6, 101 (1938); J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (New York: John Wiley & Sons, Inc., 1940), chaps. 13 and 14. See also, this volume, page 344 *et seq.*

other hand, decrease the energy, and are therefore most important at low temperatures. It follows, therefore, that at high temperatures the number of clusters of more than one molecule will be less than "normal," and at low temperatures the number will be greater than normal.

Now suppose  $n_j$  is the actual number of clusters of  $j$  molecules in a given system, and as before, let  $n_j^0$  be the normal number of such clusters. The departure of the distribution of the molecules from normal is then measured by the set of numbers

$$\begin{aligned} m_1 &= n_1 - n_1^0 + N \\ m_j &= n_j - n_j^0 \quad (j > 1) \end{aligned} \quad (15.2)$$

The great advantage of using the  $m_j$  instead of the  $n_j$  to describe the system is that it removes from consideration the "accidental" clusters which are present even if no intermolecular forces are acting. Moreover, it can be shown that within wide limits the values of the  $m_j$  are independent of  $v_0$ , while obviously the  $n_j$  depend strongly on the value assigned to  $v_0$ .

Now since the total number of molecules is  $N$ , we must have

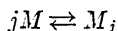
$$\begin{aligned} \Sigma j n_j &= N \\ \text{or} \quad -N + \Sigma j(n_j^0 + m_j) &= \Sigma j n_j^0 + \Sigma j m_j - N = N \end{aligned}$$

$$\text{But} \quad \Sigma j n_j^0 = N$$

$$\text{and therefore} \quad \Sigma j m_j = N \quad (15.3)$$

If there are no intermolecular forces, this definition of the  $m_j$  gives  $m_1 = N$ ,  $m_j = 0$  ( $j > 1$ ). If there were only attractive forces, the  $m_j$  would all be positive for  $j > 1$ , and  $m_1$  would be less than  $N$ ; but repulsive forces may make some  $m_j$  negative, and  $m_1 > N$ .

Mayer has shown that in practically every respect the actual properties of a gas are those of an ideal gas composed of  $m_1$  single molecules,  $m_2$  double molecules,  $m_3$  triple molecules, and so on. The total number of molecules in this equivalent ideal gas is therefore  $M = \Sigma m_j$ . The only extraordinary feature of the equivalent ideal gas is that the numbers of some varieties of molecules are negative! It has also been shown that the clusters obey the mass-action law, except that negative values of the equilibrium constant are possible. If, for example, we consider the equilibrium between single molecules and clusters of  $j$  molecules,



then

$$\frac{\left(\frac{m_j}{V}\right)}{\left(\frac{m_1}{V}\right)^j} = b_j \quad (15.4)$$

where  $b_j$  is independent of  $V$  unless the cluster  $M_j$  is so large that it occupies the whole of  $V$ .



The constants  $b_i$  of (15.4) determine all of the  $m_i$  in terms of  $m_1$ :

$$m_i = b_i(m_1)^i V^{-(i-1)} \quad (15.5)$$

so that Equation (15.3) becomes

$$\sum j b_i (m_1)^i V^{-(i-1)} = N \quad (15.6)$$

if we define  $b_1 = 1$ . If the  $b_i$  are known, this equation can be used to calculate  $m_1$ , and hence all the  $m_i$  by (15.5). However, since Equation (15.6) cannot be easily solved for  $m_1$ , it is more convenient to introduce the parameter  $Z$  defined by

$$Z = \frac{m_1}{V} \quad (15.7)$$

In terms of  $Z$ , (15.6) becomes

$$\sum j b_i V Z^i = N \quad (15.8)$$

or, if  $v$  is the volume per molecule,  $V/N$ ,

$$\sum j b_i v Z^i = 1 \quad (15.9)$$

which may be regarded as the equation determining  $Z$ . Then

$$m_i = N v b_i Z^i \quad (15.10)$$

The total number of clusters,  $n$ , is now given by

$$n = \sum m_i = \sum N v b_i Z^i \quad (15.11)$$

and, since the clusters behave like the molecules of an ideal gas,

$$\begin{aligned} P &= \frac{n k T}{V} \\ &= k T \sum b_i Z^i \end{aligned} \quad (15.12)$$

To illustrate the use of these equations let us consider the simple case of a dilute gas of rigid, non-attracting spheres of radius  $r_0$ . If we define a cluster of two molecules as two molecules whose centers are within a distance  $2r$ , the normal number of clusters of two molecules,  $n_2^0$ , can be found simply. If we consider a sphere of radius  $2r$  drawn about the center of any molecule, the probability of finding another molecule within this sphere is simply the product of the volume of the sphere by the number of molecules per unit volume, or  $\frac{4}{3}\pi r^3(N/V)$ . The total number of clusters is then  $N$  times this quantity, divided by two since each cluster has been counted twice. Hence

$$n_2^0 = \frac{1}{2} \frac{4}{3} \pi r^3 \frac{N^2}{V}$$

The actual number of clusters of two molecules, however, is smaller than this because of the fact that the closest possible distance of approach of two molecules is  $2r_0$ . Hence the actual volume within which the second molecule of a

cluster can be located is  $\frac{3}{2}\frac{4}{3}\pi(r^3 - r_0^3)$ , and the probability that a given molecule is part of a cluster is  $\frac{3}{2}\frac{4}{3}\pi(r^3 - r_0^3)N/V$ . The actual number is then

$$n_2 = \frac{1}{2}\frac{4}{3}\pi(r^3 - r_0^3) \frac{N^2}{V}$$

and

$$m_2 = n_2 - n_2^0 = -\frac{1}{2}\frac{4}{3}\pi r_0^3 \frac{N^2}{V}$$

If we let  $v'$  be the volume of a molecule,  $\frac{4}{3}\pi r^3$ , this may be written

$$m_2 = -4v' \frac{N^2}{V}$$

This number is numerically very small compared to  $N$  if  $v'$  is small compared to  $V/N$ , the volume per molecule; and the values of  $m_3$ , etc., will be still smaller. Hence  $m_1$  will be essentially  $N$ . The equilibrium constant  $b_2$  is then given by

$$\left(\frac{m_1}{V}\right) = -4v' \frac{m_2}{V}$$

The other  $b_i$  are even smaller. Equation (15.9) for the determination of  $Z$  is therefore

$$vZ + 2b_2vZ^2 + \dots = 1$$

or

$$Z = \frac{1}{v} + 8\frac{v'}{v^2} + \dots$$

Substituting this in Equation (15.12) gives

$$\begin{aligned} P &= kT(Z - 4v'Z^2 + \dots) \\ &= \frac{kT}{v} \left(1 + 4\frac{v'}{v} + \dots\right) \\ &= \frac{RT}{V} \left(1 + 4\frac{V_0}{V} + \dots\right) \end{aligned}$$

where  $V_0$  is the actual volume of one mole of molecules.

Let us now consider the behavior of a gas as its volume is made smaller and smaller. If we write Equation (15.9) in the form

$$\sum j b_j Z^j = \frac{1}{v} \quad (15.13)$$

it is obvious that for large values of  $v$  only the first few terms of the series are important, and  $Z$  varies roughly as  $1/v$ . It can be shown that in general  $Z$  always increases as  $v$  decreases. It is not, however, necessary for  $Z$  to become

infinite when  $v$  approaches zero, for, if the series on the left of (15.13) becomes divergent for any value of  $Z$ , the series has an infinite value, and  $v$  vanishes.

The ratio of any two successive terms in the series on the left of (15.13)

$$R_i = \frac{(j+1)b_{j+1}Z^{i+1}}{jb_iZ^i}$$

is simply the ratio of the numbers of molecules in clusters of  $(j+1)$  to the number in clusters of  $j$ . Since there is no reason to suppose that this ratio will change erratically as we pass from one  $j$  value to the next, it is reasonable to suppose that it will approach some definite limit as  $j$  becomes large. Actually Mayer has shown that below a definite temperature,  $T_m$ ,  $b_j$  may be expressed in the form

$$b_j = f(j)b_0^j$$

where  $b_0$  is a constant, and  $f(j)$  is a function of  $j$  which for large values of  $j$  takes the form

$$f(j) = cj^{-5/2}$$

here  $c$  is a constant. Hence for large  $j$

$$R_j = (j+1)^{3/2} b_0 Z$$

which approaches the constant value  $b_0 Z$  as  $j$  becomes large.

Now if  $Z$  is less than  $b_0^{-1}$ ,  $R_j$  becomes less than 1 as  $j$  becomes large, and the number of molecules in clusters of  $j$  becomes smaller and smaller. Hence most of the molecules will be in small clusters. If, on the other hand,  $Z$  is greater than  $b_0^{-1}$ ,  $R_j$  will become greater than 1 as  $j$  becomes large, and the number of molecules in large clusters becomes large. If  $Z$  is exactly equal to  $b_0^{-1}$ , say for  $v = v_s$ , Equation (15.13) becomes

$$\sum j f(j) = \frac{\dot{\lambda}}{v_s} \quad (15.14)$$

This series is easily seen to be convergent, so that there exists a definite volume  $v_s$  as long as the temperature is below  $T_m$ . We shall see presently that  $v_s$  is the volume per molecule in the saturated vapor. The complete behavior of Equation (15.13) is then the following: for small values of  $Z$ ,  $v = 1/Z$ ; as  $Z$  increases  $1/v$  also increases until  $Z = b_0^{-1}$  and  $v = v_s$ ; at this point there is a discontinuous break in the curve, and  $v$  falls to zero.

Actually the volume does not fall all the way to zero, for the assumption we have made that the constants  $b_j$  are independent of  $v$  breaks down before the limit is reached. As the volume decreases, the clusters become larger and larger, and eventually one cluster will occupy the whole volume. If the volume is decreased beyond this point, the cluster itself is compressed, which of course will alter its equilibrium constants. The last sentence of the preceding para-

graph must therefore be modified to say that when  $Z$  reaches the value  $b_0^{-1}$ ,  $v$  suddenly falls to a value,  $v_f$ , which though small is not zero.

Since  $Z$  is constant for all values of  $v$  between  $v_s$  and  $v_f$ , and  $P$  is given in terms of  $Z$  by (15.12), we see that  $P$  is constant for this volume range. All that happens, therefore, as  $v$  is decreased in this volume range is an increase in the number of molecules in the largest clusters. But this is just what happens when a gas liquefies: the pressure remains constant, while the number of molecules in the liquid phase increases. We may therefore conclude that  $v_s$  is the molecular volume of the saturated vapor, and  $v_f$  is the volume of the liquid. One interesting fact arises. The number of molecules per unit volume in small clusters is the same in the liquid as in the saturated vapor. We, therefore, can regard the vapor pressure of a liquid as being due to the fact that the liquid is a saturated solution, with its own vapor as the solute.

Mayer's theory therefore does what no previous theory of imperfect gases has done—it predicts directly the phenomenon of condensation. Its usefulness, however, depends on the possibility of evaluating the equilibrium constants  $b_i$ . The calculation of these constants in terms of the intermolecular forces is a problem of great mathematical difficulty, but nevertheless much progress has been made toward its solution. In particular, the relationships are known between the  $b_i$  and the virial coefficients  $A_k$ , in the equation

$$PV = RT \left( 1 + \frac{A_1}{V} + \frac{A_2}{V^2} + \cdots \right)$$

which has been used as an empirical equation to describe the pressure-volume relationship for gases at moderate pressures. Unfortunately it is also known that the phenomenon of condensation is not determined primarily by the early terms in this series, but by the late ones, so that there is no justification for trying to express the properties of liquids in terms of an equation of state extrapolated from low pressures. The failure of such equations of state as that of van der Waals to give good results for condensation phenomena is well known.

(16) **The Critical Point:** If a gas is compressed at constant temperature it may behave in either of two ways. It may be that as the volume is decreased,

the pressure always increases, so that at all points  $\left( \frac{\partial P}{\partial V} \right)_T < 0$ . Alternatively,

there may be a region in which  $\left( \frac{\partial P}{\partial V} \right)_T > 0$ . It is a well known experi-

mental fact that there exists a characteristic temperature for each gas,  $T_c$ , above which the first behavior is always observed, and below which the second is observed. It is found that for the temperature  $T_c$  itself, there is a single

volume,  $V_c$ , and pressure,  $P_c$ , at which  $\left( \frac{\partial P}{\partial V} \right)_T = 0$ . For all other volumes

on this isotherm  $\left( \frac{\partial P}{\partial V} \right)_T < 0$ . We shall define the state of the gas at which  $T = T_c$ ,  $V = V_c$ , and  $P = P_c$  as the critical state of the gas, and the tempera-

ture  $T_c$ , volume  $V_c$  and pressure  $P_c$  as the critical temperature, volume, and pressure.

Now let us consider the same quantity of gas compressed to the volume  $V_c$ , but at a temperature well below  $T_c$ . On examination it is always found that the gas has partially liquefied, so that two definite phases are present, with a sharp boundary between them. If the system is now slowly heated, the meniscus between the two phases remains in very nearly the same place until the temperature reaches the neighborhood of  $T_c$ . At some temperature in this neighborhood, the meniscus suddenly seems to broaden and the whole vessel becomes opalescent. If the temperature is raised a little more the vessel becomes clear again, but now there seems to be only one phase present.

Until very recently it was taken as axiomatic that the temperature,  $T_m$ , at which the meniscus disappeared, was identical with the critical temperature,  $T_c$ . Recent theoretical and experimental work, however, have both indicated that this may not be the case, and that  $T_m$  may actually be lower than  $T_c$ . The experimental evidence is due largely to Maass<sup>1</sup> and his coworkers. Perhaps the simplest evidence is that obtained from the heating of a liquid-vapor mixture at a volume not quite equal to the critical volume. Suppose for the sake of definiteness that the volume  $V$  is a little less than the critical volume, and that the sample contains exactly one mole. At the original temperature the molar volume of the liquid must be smaller than  $V$ , and that of the vapor greater than  $V$ . As the temperature is increased, both of these molar volumes approach  $V_c$ . At some stage, therefore, the molar volume of the liquid must be equal to  $V$ , the volume of the container. At this point the liquid phase must fill the whole container. Experimentally, this means that, on heating, the meniscus moves upward in the tube until finally it reaches the top and the vapor phase vanishes. Further heating then corresponds to the heating of a one-phase system, and the critical point can not be observed. Similarly, if the volume of the system is a little greater than the critical volume, the meniscus should move to the bottom of the tube, and the liquid phase should disappear before the critical point is reached.

We must therefore conclude that if the temperature  $T_m$  is the same as  $T_c$ , the meniscus should disappear in the middle of the tube only if the volume is *exactly* equal to the critical volume—a condition which can not be attained experimentally. It is found, however, that there is a very definite range of volumes over which the disappearance of the meniscus can be observed. It therefore follows that the meniscus disappears *before* the critical temperature is reached.

A number of other explanations of this phenomenon have been advanced. Verschaffelt<sup>2</sup> has suggested that the effect is due to impurities, but careful

<sup>1</sup> J. S. Tapp, E. W. R. Steacie, and O. Maass, *Can. J. Research*, **9**, 217 (1933); H. S. Sutherland and O. Maass, *ibid.*, **5**, 48 (1931); C. H. Holder and O. Maass, *ibid.*, **15B**, 345 (1937); H. L. Callendar, *Proc. Roy. Soc.*, **A120**, 460 (1928); C. A. Winkler and O. Maass, *Can. J. Research*, **9**, 613 (1933); O. Maass and A. L. Geddes, *Phil. Trans. Roy. Soc.*, **A236**, 303 (1937).

<sup>2</sup> J. E. Verschaffelt, *Comm. Phys. Lab., Leiden*, Supp. No. 10 (1904). See also J. Traube, *Z. Elektrochem.*, **9**, 619 (1903).

analysis shows that although the effect of impurities is present, it is inadequate to explain all of the experimental facts. It has also been suggested that the reason the meniscus does not move to the end of the tube is due to the slowness with which equilibrium is attained near the critical point, but since some experiments have been carried out in which the heating was done at the rate of  $0.1^\circ$  per day this too does not seem to be the most reasonable explanation.

Maass has investigated the region between  $T_m$  and  $T_c$  very carefully. He finds that, although there is no visible meniscus, there is still a difference in density between the material at the top of the tube and that at the bottom. These density differences, moreover, were unaffected by stirring and persisted over periods of time as long as six hours. At the same time other properties, such as solubility and dielectric constant, all showed sharp changes at the temperature  $T_m$ .

Many of these effects have been explained by Mayer's theory of condensation. We have already seen that condensation will take place when the series  $\sum v b_i Z^i$  diverges. As long as  $b_i$  can be put in the form  $f(j)b_i'$ , this divergence is sure to happen for some value of  $Z$ . Above the temperature  $T_m$ , however, this form for  $b_i$  no longer holds. This is in itself no indication that the series  $\sum v b_i Z^i$  does not converge so that it may be that condensation will take place at temperatures above  $T_m$ . Mayer has shown that this is indeed the case, and that condensation is still possible up to a temperature  $T_c$ , higher than  $T_m$ . Mayer's theory therefore predicts three, rather than two, types of behavior for a gas on isothermal compression. Below  $T_m$  we have the ordinary type on condensation, beginning when the molecular volume is reduced to  $v_s$ . In particular the value of  $\left(\frac{\partial P}{\partial V}\right)_T$  at this point changes discontinuously from a negative value to 0. Between  $T_m$  and  $T_c$ , on the other hand, condensation still begins when the molecular volume is reduced to a certain value  $v_s$ , but in this range the value of  $\left(\frac{\partial P}{\partial V}\right)_T$  is continuous at this point, i.e., the isothermals on a  $p$ - $v$  diagram become flat, but without the sharp break which is found below  $T_m$ . Finally, above the temperature  $T_c$  there is no condensation, and  $\left(\frac{\partial P}{\partial V}\right)_T$  is negative everywhere.

Some typical isothermals in the neighborhood of the critical point are shown in Fig. 7. To the right of the shaded regions the system is entirely gaseous; to the left, liquid. The lower shaded region corresponds to the ordinary region of stability of two-phase liquid-vapor systems. It is bounded on the top by the isothermal for the temperature  $T_m$ . At  $T_m$  the surface tension, and hence the meniscus, of the liquid phase disappears; and simultaneously there are abrupt changes in many other properties of the liquid. A system in the upper shaded portion of the diagram is still a two-phase system, the molar volumes of the phases being given in the usual way by abscissae at the two boundaries of the shaded region.

Whether the condensed phase in the region between  $T_m$  and  $T_c$  should be called the liquid is an open question. In most respects it resembles a highly compressed gas, rather than the ordinary conception of a liquid. Moreover there are some indications that the transition which takes place at  $T_m$  for the

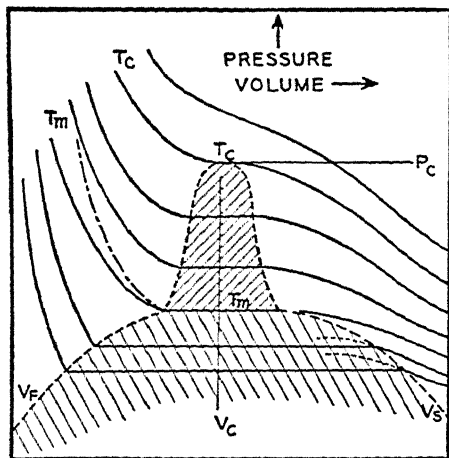


FIG. 7. Pressure-Volume Relationships in the Neighborhood of the Critical Point

liquid in equilibrium with its vapor extends to the left through the liquid region. This possible transition is indicated in Fig. 7 by the dash-dot line. If this transition line is real, it offers a convenient division between the liquid state and the gaseous state, and the old idea of continuity between liquid and gas can be abandoned. If this point of view is taken, the condensation phenomena which occur between  $T_m$  and  $T_c$  are to be regarded as a transition from one gas phase to another.

It is evident from the generality of the above description that there is still much to be done both experimentally and theoretically on critical phenomena. The continuation of the transition at  $T_m$  into the liquid region is based on experimental, rather than theoretical, considerations although there are indications in Mayer's theory which may lead to it. Moreover the sharp break in the  $p$ - $v$  curve for the liquid in equilibrium with its vapor is predicted by Mayer's theory, but has not been observed. The theory unfortunately does not as yet predict quantitatively how great the change in slope at  $T_m$  should be, and it may be below the limit of experimental error.

(17) **Liquid Flow:** As we have stated before, no liquid can permanently resist a shearing stress. If such a stress is applied to any liquid, flow will take place, and continue until the stress is removed.

Experimentally it is found that the rate of flow is proportional to the shearing stress. Let us consider, for example, the simple arrangement shown in Fig. 8. The lower line in this figure represents a fixed plate of area  $A$ , the upper line a similar movable plate of the same area, at a distance  $a$  from the lower plate. The space between the plates is supposed to be filled with liquid. If a force  $F$  is applied to the upper plate, it is found that the upper plate will

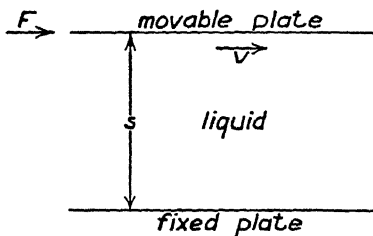


FIG. 8. Flow between Two Moving Plates.

move with a velocity  $v_0$ , which is proportional to  $F$  (provided  $F$  is not too large) and to  $a$ , and inversely proportional to  $A$ . We may, therefore, write

$$v_0 = \varphi Fa/A \quad (17.1)$$

where  $\varphi$  is a constant, characteristic of the liquid, which is known as the fluidity. It is also found that the velocity of the liquid between the plates is proportional to the distance  $z$  from the lower plate, so that  $\frac{dv}{dz}$  is a constant and equal to  $v_0/a$ . The ratio  $F/A$  is by definition the shearing stress,  $s$ , so that Equation (17.1) can be written

$$\frac{dv}{dz} = \varphi s \quad (17.2)$$

It is more customary to use the reciprocal of the fluidity, the viscosity,  $\eta$ , defined by

$$\eta = 1/\varphi \quad (17.3)$$

than to use  $\varphi$  itself. In terms of  $\eta$ , Equation (17.2) becomes

$$s = \eta \frac{dv}{dz} \quad (17.4)$$

In practice the flow of a liquid between parallel plates is difficult to realize. A much more convenient experimental arrangement consists of two concentric cylinders with the liquid between them. The outer cylinder is caused to rotate with a constant angular velocity  $\Omega$ . This rotation is transmitted through the liquid to the inner cylinder, and produces a torque tending to rotate it at the same speed as the outer cylinder. By measuring the torque necessary to keep the inner cylinder from rotating, the viscosity of the liquid can be computed.

Figure 9 shows a cross section of the two cylinders perpendicular to their common axis. In order to keep the outer cylinder rotating at constant speed, a torque  $L$  must be applied. This torque must be equal and opposite to that required to hold the inner cylinder stationary, for otherwise the whole system would show an angular acceleration. Let us now consider the fluid friction over a cylindrical surface of radius  $r$ . The liquid outside this surface tends to drag the liquid inside after it in its motion, and the liquid inside tends to slow down the liquid outside. There will, therefore, be a torque exerted by each part of the liquid on the other. Since the total torque on any part of the system must vanish,

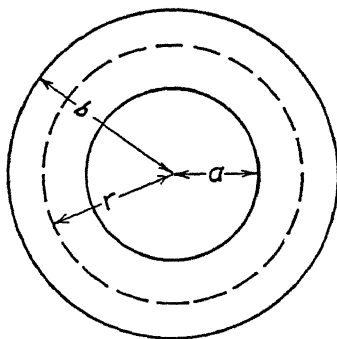


FIG. 9. Flow between Rotating Cylinders.



each of these torques must also be of magnitude  $L$ . We therefore conclude that the frictional torque across any cylindrical surface in the liquid, no matter what its radius may be, is always equal to  $L$ .

This torque can be calculated from Equation (17.3). It is necessary, however, to use some caution in interpreting the derivative  $\frac{dv}{dz}$ . It is tempting to put in for this derivative simply  $\frac{dv}{dr}$ , but the velocity  $v$  is the product of the angular velocity  $\omega$  by the radius  $r$ . Hence

$$\frac{dv}{dr} = \frac{d(r\omega)}{dr} = r \frac{d\omega}{dr} + \omega$$

To include the last term in the expression would lead to a viscous torque even if the liquid were all rotating with the same angular velocity, which is manifestly absurd. A detailed discussion of this problem<sup>1</sup> shows that this term should be omitted, and the  $\frac{dv}{dz}$  should be replaced by  $r \frac{d\omega}{dr}$ . The frictional stress per unit area across any surface element is therefore  $\eta r \frac{d\omega}{dr}$ . The total torque  $L$  is the product of this by the area of the cylindrical surface,  $2\pi r l$ , where  $l$  is the length of the cylinder, and by the lever arm,  $r$ . Hence

$$L = 2\pi\eta l r^3 \frac{d\omega}{dr} \quad (17.5)$$

Since  $L$  is constant, this equation may be integrated to give

$$\omega = \frac{L}{2\pi\eta l} \left( C - \frac{1}{2r^2} \right) \quad (17.6)$$

where  $C$  is the constant of integration. At the boundary of the inner cylinder,  $r = a$ , and  $\omega = 0$ , hence

$$0 = \frac{L}{2\pi\eta l} \left( C - \frac{1}{2a^2} \right) \quad (17.7)$$

Eliminating  $C$  between (17.6) and (17.7) gives

$$\omega = \frac{L}{4\pi\eta l} \left( \frac{1}{a^2} - \frac{1}{r^2} \right) \quad (17.8)$$

At the outer cylinder,  $r = b$  and  $\omega = \Omega$ , so that

$$\Omega = \frac{L}{4\pi\eta l} \left( \frac{1}{a^2} - \frac{1}{b^2} \right) \quad (17.9)$$

<sup>1</sup> L. Page, *Introduction to Theoretical Physics* (New York: D. Van Nostrand Co., Inc., 1928), p. 231.

or

$$L = 4\pi\eta l\Omega \frac{a^2b^2}{b^2 - a^2} \quad (17.10)$$

By measuring  $L$ ,  $\Omega$ ,  $a$ ,  $b$ , and  $l$ , this equation may be used to find  $\eta$ .

A second common method for the determination of viscosities involves the rate of flow of liquids through capillary tubes. If the flow is sufficiently slow that turbulence does not set in, the liquid moves parallel to the length of the tube, fastest in the center, and with zero velocity at the wall. As the concentric shells of liquid move along, the friction between them resists the driving force of the pressure gradient. The total rate of flow is thus determined by the pressure drop in the tube, and the viscosity of the liquid.

In Fig. 10 is shown a cross section of a tube of radius  $a$  along which a liquid is moving in the manner just described. Let  $v$  be the velocity of flow at a distance  $r$  from the axis of the tube. If we consider a cylindrical shell of fluid bounded by the cylinders of radii  $r$  and  $r + dr$ , this shell is acted on by three forces: the excess of the pressure on one end over that on the other, and the forces of friction on the inner and outer surfaces. The first of these is simply the product of the end area by the pressure drop  $p$ , or  $2\pi r p dr$ . On the inner surface the stress is given by Equation (17.4) in a direction tending to force the liquid along the tube. On the outer surface the stress is

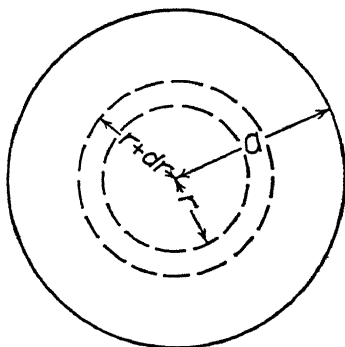


FIG. 10. Axial Flow in a Tube.

$$s + ds \quad \eta \left[ \frac{dv}{dr} + \frac{d}{dr} \left( \frac{dv}{dr} \right) dr \right]$$

in the opposite direction. Hence the total frictional force on the inner surface is

$$2\pi r l \eta \frac{dv}{dr}$$

where  $l$  is the length of the tube, while the force on the outer surface is

$$2\pi(r + dr)l\eta \left[ \frac{dv}{dr} + \frac{d}{dr} \left( \frac{dv}{dr} \right) dr \right]$$

or, to the first order of infinitesimals,

$$2\pi r l \eta \frac{dv}{dr} + 2\pi l \eta \frac{dv}{dr} dr + 2\pi l \eta r \frac{d^2v}{dr^2} dr$$

The total force acting on the shell must vanish when the flow is steady, so that

$$2\pi r p dr - 2\pi r l \eta \frac{dv}{dr} + 2\pi r l \eta \frac{dv}{dr} + 2\pi l \eta \frac{dv}{dr} dr + 2\pi l \eta r \frac{d^2v}{dr^2} dr = 0$$

or

$$\begin{aligned} -rp &= l\eta \left[ \frac{dv}{dr} + r \frac{d^2v}{dr^2} \right] \\ &= l\eta \frac{d}{dr} \left[ r \frac{dv}{dr} \right] \end{aligned}$$

Integrating, we have

$$-\frac{1}{2}r^2p = l\eta r \frac{dv}{dr} + C_1$$

where  $C_1$  is a constant of integration. Dividing through by  $r$  and integrating a second time gives

$$-\frac{1}{4}r^2p = l\eta v + C_1 \ln r + C_2 \quad (17.11)$$

where  $C_2$  is a second constant of integration. Since the velocity is not infinite at  $r = 0$ ,  $C_1$  must vanish. To determine  $C_2$  we use the condition that  $v = 0$  for  $r = a$ , or

$$-\frac{1}{4}a^2p = C_2$$

Substitution of this expression for  $C_2$  in (17.11) gives

$$v = \frac{1}{4l\eta} (a^2 - r^2)p \quad (17.12)$$

The total volume of the liquid carried through the tube per second is therefore

$$\begin{aligned} V &= \int_0^a 2\pi r v dr \\ &= \frac{4a^4p}{8l\eta} \end{aligned} \quad (17.13)$$

Hence a measurement of  $V$ ,  $p$ ,  $a$ , and  $l$  determines  $\eta$ .

Both of these methods of measuring viscosity are subject to two important limitations. In the first place they must be carried out at sufficiently low speeds so that the flow is not turbulent, or the assumption of stream-line flow which has been used in these derivations breaks down. The second limitation lies in the assumption that the liquid in contact with a surface is at rest relative to the surface. This assumption seems to be justified for most liquids, at least if the speeds are not too high nor the viscosity too great. With gases, however, the problem of slippage at the surface is often important, and difficult to correct for in actual cases (see p. 91) *et seq.*

For most liquids (sulfur being a conspicuous exception) the viscosity decreases rapidly with increasing temperature. The observed data may be fitted

quite well by an equation of the form

$$\eta = Ae^{E/RT} \quad (17.14)$$

or

$$\varphi = A^{-1}e^{-E/RT} \quad (17.15)$$

The form of Equation (17.15) suggests that  $E$  is some sort of activation energy which must be overcome for flow to take place. This idea has been developed further by Eyring and his coworkers.<sup>2</sup>

These authors assume that flow can not take place in a liquid except by molecules which find themselves next to a hole in the structure of the liquid. This hole does not need to be as large as a molecule, for if there is sufficient room for a pair of molecules to revolve together about the point midway between them, as shown in Fig. 11, such a motion is of a type which can produce flow.

To form a hole of molecular dimensions in a liquid should require an energy of the order of magnitude of the heat of vaporization of the liquid. If  $\epsilon$  is the total strength of all the binding forces holding a molecule in a liquid, the energy of vaporization of the liquid per mole will be  $N\epsilon/2$ , the factor  $\frac{1}{2}$  arising because each binding force acts between two molecules. If we vaporize just one mole-

cule from the interior of the liquid, leaving behind a hole, the energy required is the difference between  $N\epsilon$ , the energy required to vaporize a mole of liquid leaving behind the holes originally occupied by the molecules, and  $N\epsilon/2$ , the energy required to vaporize a mole of liquid without leaving holes. The difference is  $\frac{N\epsilon}{2}$ . We therefore conclude that if the holes required for viscous

flow are of the same size as the molecules, the activation energy of flow should be exactly equal to the energy of vaporization.

The actual activation energies as computed by Equation (17.14) or (17.15) are smaller than the energy of vaporization by a factor of 3 or 4. Ewell and Eyring account for this by the assumption that the holes are of smaller than molecular dimensions and that for the most part the flow takes place by the

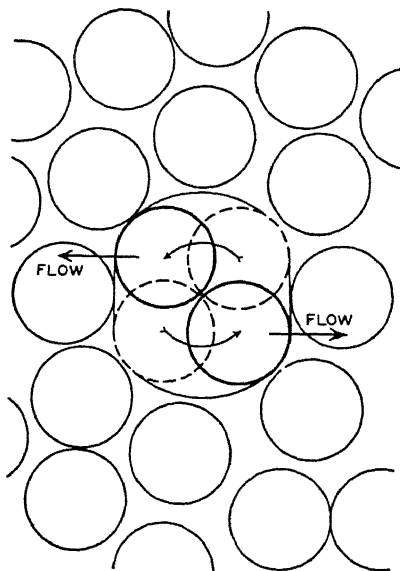


FIG. 11. Viscous Flow by Rotations of Double Molecules.

<sup>2</sup> H. Eyring, *J. Chem. Phys.*, 4, 283 (1936); R. H. Ewell and H. Eyring, *J. Chem. Phys.*, 5, 726 (1937); J. Hirschfelder, D. Stevenson, and H. Eyring, *J. Chem. Phys.*, 5, 896 (1937).

cooperative method illustrated in Fig. 11. For molecules which are roughly spherical, the activation energy of flow seems to be very nearly one third of the heat of vaporization, while for long chain molecules the activation energy seems to be only about one quarter of the heat of vaporization.

Eyring and his coworkers have also attempted to explain the values of the constant  $A$  of Equation (17.14) on the basis of Eyring's<sup>3</sup> theory of absolute reaction rates of chemical reactions. If we consider a small portion of the liquid, we may suppose the molecules to be arranged nearly in a regular space lattice. Let us therefore consider a unit cell of the lattice. Let the area of the face of the unit cell parallel to the plane of flow be  $\sigma$ , and the altitude of the unit cell perpendicular to this face be  $\delta$ . If we suppose the unit cell to contain just one molecule, the volume  $\sigma\delta$  of the cell, is simply  $v_0$ , the molecular volume. Relative to the molecules in the plane of the base of the cell, a molecule in the upper face moves with a mean velocity  $u = \delta(\partial v/\partial z)$  if  $z$  is the coordinate in the direction perpendicular to the cell base. This motion, however, is far from uniform. For the most part it consists of a rapid vibration within the space to which it is confined by the surrounding molecules. Occasionally the molecule will break through this barrier and occupy a new position of equilibrium. Let  $\lambda$  be the distance between these successive positions of equilibrium. Between them lies a potential energy barrier, of height  $E$ , practically equal to the activation energy of flow.

If there is no shearing stress on the liquid, the molecules will jump equally often in all directions. A shearing stress, on the other hand, has the effect of lowering the potential barrier in one direction, and raising it in the opposite direction. The molecules will therefore jump more frequently in the direction of the stress, and less frequently in the opposite direction, and hence flow takes place. If the shearing stress is  $s$ , the force on a single molecule is the product  $s\sigma$  of the stress and the area occupied by one molecule. If the barriers between equilibrium positions are symmetrical, the distance from an equilibrium position to the top of the barrier is  $\lambda/2$ , and the work done by the stress on a molecule in moving to the top of the barrier is  $s\sigma\lambda/2$ . This then is the amount by which the potential energy at the top of the barrier is lowered in the direction of the stress, and raised in the opposite direction.

Eyring's absolute rate theory gives as the rate at which molecules cross a barrier of this kind

$$\frac{kT}{h} \frac{Q^*}{Q} e^{-E/kT}$$

where  $Q$  is the partition function for a molecule at a position of equilibrium, and  $Q^*$  is the partition function for a molecule at the top of the barrier. If we assume that the crossing of the barrier affects only the degree of freedom in the direction of the motion, and that the motion around the position of equilibrium

<sup>3</sup> H. Eyring, *J. Chem. Phys.*, **3**, 107 (1935); W. F. K. Wynne-Jones and H. Eyring, *ibid.*, **3**, 492 (1935).

is a simple translation in a box of edge  $V_f^{1/3}$  where  $V_f$  is the free volume per molecule,

$$Q^* = \frac{h}{(2\pi mkT)^{1/2} V_f^{1/3}}$$

and the rate of crossing

$$K = \left( \frac{kT}{2\pi m} \right)^{1/2} \frac{1}{V_f^{1/3}} e^{-E/kT} \quad (17.16)$$

In the direction of flow the  $E$  of this expression is  $E - s\sigma\lambda/2$ , and in the opposite direction  $E + s\sigma\lambda/2$ . The excess of the forward rate over the backward rate is therefore

$$\left( \frac{kT}{2\pi m} \right)^{1/2} \frac{1}{V_f^{1/3}} \left( e^{-\frac{E-s\sigma\lambda/2}{kT}} - e^{-\frac{E+s\sigma\lambda/2}{kT}} \right) = 2 \left( \frac{kT}{2\pi m} \right)^{1/2} \frac{1}{V_f^{1/3}} e^{-E/kT} \sinh \frac{s\sigma\lambda}{2kT}$$

Ordinarily  $\frac{s\sigma\lambda}{2kT}$  is small compared to unity, so that  $\sinh \frac{s\sigma\lambda}{2kT}$  is approximately equal to  $\frac{s\sigma\lambda}{2kT}$ , and the net rate may be written

$$\left( \frac{kT}{2\pi m} \right)^{1/2} \frac{1}{V_f^{1/3}} \frac{s\sigma\lambda}{kT} e^{-E/kT}$$

Since each jump represents a net advance of a distance  $\lambda$ , the mean forward velocity,  $u$ , is  $\lambda$  times this expression, or

$$u = \frac{s\sigma\lambda^2}{(2\pi mkT)^{1/2} V_f^{1/3}} e^{-E/kT}$$

But, since  $u = \delta \frac{\partial v}{\partial z}$

$$\frac{\partial v}{\partial z} = \frac{s\sigma\lambda^2}{(2\pi mkT)^{1/2} V_f^{1/3}} e^{-E/kT}$$

and since  $s = \eta \frac{\partial v}{\partial z}$  by the definition of  $\eta$ ,

$$\eta = (2\pi mkT)^{1/2} V_f^{1/3} \frac{v}{\sigma\lambda^2} e^{E/kT} \quad (17.17)$$

In the special case of a simple cubic lattice,  $\lambda$  might be taken equal to  $\delta$ , and  $\sigma$  to  $\delta^2$ , so that we would have

$$\eta = (2\pi mkT)^{1/2} V_f^{1/3} \frac{v}{\delta^3} e^{E/kT} \quad (17.18)$$

or, since  $\delta^3$  would then be equal to  $v_0$ , the volume per molecule,

$$\eta = (2\pi mkT)^{1/2} \frac{V_f^{1/3}}{v_0} e^{E/kT} \quad (17.19)$$

In view of the many approximations involved in the derivation of Equation (17.19) it is hardly surprising that it does not agree too well with experiment. The comparison can be carried out in two different ways. The first method would be to make a direct comparison between the value of  $\eta$  calculated by Equation (17.19) with the experimental value of  $\eta$ . This, however, involves making estimates of  $E$  and  $V_f$ , neither of which is too well known. Since the value of  $\eta$  is very sensitive to the value of  $E$ , this would hardly be a fair com-

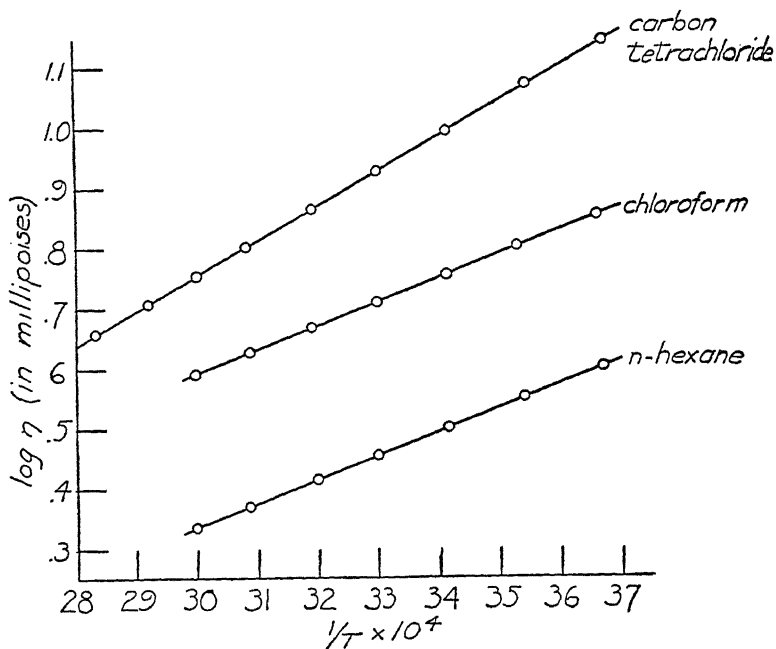


FIG. 12. Variation of Viscosity with Temperature for Typical Liquids.

parison. A second method of comparison is possible by means of a plot of  $\ln \eta$  against  $1/T$ . The theory predicts that such a plot should give a straight line, whose slope is  $E/R$ . The straightness of the plot offers one check on the theory, and the comparison of the value found for  $E$  with the heat of evaporation offers a second check. It will be noted, however, that this method gives no evidence on the value of the factors in Equation (17.19). It is actually found that a plot of  $\ln \eta$  against  $1/T$  does give a straight line. Several such plots are shown in Fig. 12. A comparison of the activation energy  $E$  for flow, and  $\Delta H_{\text{vap}}$  for a number of liquids is shown in Table VII. It will be noted that the ratio  $n = \Delta H_{\text{vap}}/E$  ranges only from about 2.5 to about 4.5.

The principal deviations from this relationship are found, as usual, among the associated liquids. In these it is found that the viscosity is much higher than would be expected on this simple theory. This is undoubtedly due to the

effect of hydrogen bonding, or some similar effect. At high temperatures, the effect of these bonds becomes less important, and the viscosities of these liquids become nearly normal. In sulfur, on the other hand, the plot of  $\ln \eta$  against  $1/T$  shows a definite discontinuity, which can be explained by the breaking up

TABLE VII \*

Liquid	$E$ , cal/mole	$\Delta E_{\text{vap}}$ at B. P., cal/mole	$\frac{\Delta E_{\text{va}}}{E}$
$\text{CCl}_4$ .....	2,500	6,600	2.66
$\text{C}_6\text{H}_6$ .....	2,540	6,660	2.62
Cyclohexane.....	2,890	6,700	2.32
$\text{CH}_4$ .....	719	1,820	2.53
A.....	516	1,420	2.75
$\text{N}_2$ .....	449	1,210	2.70
CO.....	466	1,310	2.80
$\text{O}_2$ .....	398	1,470	3.69
$\text{C}_2\text{H}_4\text{Cl}_2$ .....	2,270	6,930	3.05
$\text{C}_2\text{H}_4\text{Br}_2$ .....	2,590	7,890	3.04
Pentane.....	1,580	5,510	3.50
Hexane.....	1,715	6,220	3.61
$\text{CHCl}_3$ .....	1,760	6,630	3.76
$\text{C}_2\text{H}_5\text{I}$ .....	1,720	6,400	3.72
$\text{C}_2\text{H}_5\text{Br}$ .....	1,585	6,080	3.84
$\text{CS}_2$ .....	1,280	5,920	4.63
$\text{C}_6\text{H}_5\text{CH}_3$ .....	2,120	7,240	3.42
Ether.....	1,610	5,700	3.54
Acetone.....	1,655	6,400	3.86
$\text{C}_2\text{H}_4$ .....	793	3,500	4.41

\* Modified from R. H. Ewell and H. Eyring, *J. Chem. Phys.*, 5, 730 (1937).

(into long chain molecules) of the  $\text{S}_8$  rings found in the low temperature forms of sulfur.<sup>1</sup>

(18) **Diffusion:** The first kinetic theory of diffusion was developed by Einstein<sup>2</sup> on the basis of osmotic pressure. Consider a liquid containing a solute which is not uniformly distributed through the solvent. If the concentration of the solute at any point is  $c$ , then (assuming the solution to be ideal) the partial molar free energy of the solute is

$$\bar{F} = \bar{F}^\circ + RT \ln c \quad (18.1)$$

The work done in transporting a mole of solute molecules through a small

<sup>1</sup> B. E. Warren and J. Burwell, *J. Chem. Phys.*, 3, 6 (1935).

<sup>2</sup> A. Einstein, *Ann. Physik*, 17, 549 (1905); *ibid.*, 19, 371 (1906); *Z. Elektrochem.*, 14, 235 (1908).



distance  $dx$  is then

$$-d\tilde{F} = -\frac{RT}{c} \frac{\partial c}{\partial x} dx \quad (18.2)$$

Hence the effective force per mole on the solute due to the concentration gradient  $\frac{\partial c}{\partial x}$  is

$$-\frac{RT}{c} \frac{\partial c}{\partial x} \quad (18.3)$$

and the force on a single molecule is

$$F_1 = -\frac{kT}{c} \frac{\partial c}{\partial x} \quad (18.4)$$

This force tends to drive the molecules in the direction of lower concentration, and therefore to wipe out the concentration gradient. It is opposed by the force of friction between the solute molecules and the solvent. If the solute molecules are large, this force of friction can be approximately calculated from Stokes' law, which gives as the opposing force

$$F_2 = 6\pi\eta rv \quad (18.5)$$

where  $\eta$  is the viscosity of the solvent,  $r$  is the radius of the solute molecule (assumed spherical), and  $v$  is the velocity of the solute molecule. At equilibrium, the two forces given by (18.4) and (18.5) are equal, so that

$$6\pi\eta rv = -\frac{kT}{c} \frac{dc}{dx}$$

or

$$v = -\frac{kT}{6\pi\eta rc} \frac{dc}{dx} \quad (18.6)$$

The total number of molecules crossing a unit area per unit time is

$$N = vc = -\frac{kT}{6\pi\eta r} \frac{dc}{dx} \quad (18.7)$$

The diffusion coefficient  $D$  is defined by the equation

$$N = -D \frac{dc}{dx} \quad (18.8)$$

Comparison of (18.8) with (18.7) leads to

$$D = \frac{kT}{6\pi\eta r} \quad (18.9)$$

which is Einstein's result. It has been applied with considerable success to the diffusion of particles of microscopic size. There is considerable doubt, however, whether it can be applied to particles of molecular dimensions, for

which the fundamental assumptions in the derivation of Stokes's law break down completely.

The problem of diffusion has been considered also by Eyring in the same way as that in which he considered viscosity. Eyring supposes the solute molecules to take the places of some of the solvent molecules in the locally regular lattice of the liquid. At intervals, the solute molecules will penetrate the barriers surrounding them, and take up new positions. The frequency with which this happens is given, as in the case of viscous flow, by Equation (17.16) of the previous section. If we now consider two layers of the liquid at a distance  $\lambda$  apart, the total number of solute molecules crossing from layer 1 to layer 2 in unit time is given by the product of the number of solute molecules per unit area of the surface,  $\lambda c_1$ , where  $c_1$  is the concentration of solute molecules in layer 1, by the frequency given in Equation (17.16), or

$$\lambda c_1 \left( \frac{kT}{2\pi m} \right)^{1/2} \frac{1}{V_f^{1/3}} e^{-E/kT}$$

The number passing in the opposite direction is given by

$$\lambda c_2 \left( \frac{kT}{2\pi m} \right)^{1/2} \frac{1}{V_f^{1/3}} e^{-E/kT}$$

so that the net rate of crossing is

$$N = \lambda(c_1 - c_2) \left( \frac{kT}{2\pi m} \right)^{1/2} \frac{1}{V_f^{1/3}} e^{-E/kT}$$

But  $c_2 = c_1 + \lambda \frac{dc}{dx}$ , so that the rate of crossing may be written

$$N = -\lambda^2 \frac{dc}{dx} \left( \frac{kT}{2\pi m} \right)^{1/2} \frac{1}{V_f^{1/3}} e^{-E/kT} \quad (18.10)$$

Comparing this with Equation (18.8) we see that

$$D = \lambda^2 \left( \frac{kT}{2\pi m} \right)^{1/2} \frac{1}{V_f^{1/3}} e^{-E/kT} \quad (18.11)$$

If this is compared with the expression for the viscosity given by Equation (17.19) of the previous section, we see that we may write

$$\frac{\lambda^2 kT}{v_0 \eta} \quad (18.12)$$

This equation, like Einstein's, predicts that the diffusion coefficient is inversely proportional to the viscosity. The factor  $1/6\pi r$  of the Einstein equation, however, is replaced by the factor  $\lambda^2/v_0$ . These two factors are of the same order of magnitude, and it is very difficult to decide which is preferable. The Eyring equation is probably nearer the truth when the solute and solvent molecules are of nearly the same size.

The exponential character of the dependence of the diffusion coefficient on the temperature has been studied carefully by Taylor.<sup>2</sup> The available data are rather meagre. The most extensive data are those of Scheffer and Scheffer<sup>3</sup> on mannitol solutions in water. Since mannitol may be expected to form hydrogen bond polymers, these data do not provide a really good test of the theory. Nevertheless the plot of  $\log D$  against  $1/T$  in this case is not far from linear, and the calculated values of the activation energy for diffusion are reasonable, ranging from 6,590 cal to 3,774 cal. The data of Cohen and Bruins<sup>4</sup> on the diffusion of tetrabromomethane in tetrachlorethane solutions, although available over a smaller temperature range, give a far more constant value of the activation energy  $E$ . The plot of  $\log D$  against  $1/T$  gives an excellent straight line corresponding to an  $E$  value of 3,490 cal. It is interesting to note, however, that this is somewhat higher than the activation energy for viscous flow in pure tetrachlorethane, which is 2,995 cal. It is therefore not surprising that the activation energy of diffusion of tetrabromomethane in tetrachlorethane should lie between these values.

(19) **Surface Tension:** It is a fundamental property of liquid surfaces that they have a tendency to contract. A raindrop, for example, tends to assume the shape of a sphere, which has a smaller area of surface than any other solid figure of the same volume. Soap bubbles stretched on wire frames assume the surface of minimum area bounded by the frames.<sup>1</sup> The same is true of the interface between two immiscible liquids, so that a drop of one liquid immersed in a second takes on a spherical form.

Because of this contractile tendency, if a liquid surface is cut along any line, it is necessary to apply a force to the two separated sections if equilibrium is to be maintained. This force is proportional to the length of the cut, and is therefore measured in terms of the force per unit length which must be applied to both sides of the boundary. The force per unit length so defined is the surface tension, and will be denoted by  $\gamma$ . It is commonly expressed in dynes per centimeter.

The existence of this surface tension suggests that the surface of a liquid may be regarded as a stretched membrane enclosing the bulk of the liquid. The analogy, however, is poor, for an ordinary membrane possesses a tension which increases as its area is increased. The tension in a liquid surface does not have this property. No matter how a liquid surface is deformed, the surface tension remains constant at all times.

Since the dimensions of surface tension are the same (mass  $\div$  time<sup>2</sup>) as those of energy per unit area, it is possible, and frequently advantageous, to think of surface tension as such an energy. The same result may be obtained more formally by considering the work necessary to change the area of a liquid

<sup>2</sup> H. S. Taylor, *J. Chem. Phys.*, 6, 331 (1938).

<sup>3</sup> J. D. R. Scheffer and F. E. C. Scheffer, *Proc. Acad. Sci. Amsterdam*, 19, 148 (1916).

<sup>4</sup> E. Cohen and H. P. Bruins, *Z. physik. Chem.*, 103, 404 (1923).

<sup>1</sup> C. H. Boys, *Soap Bubbles and the Forces which Mold Them* (New York: E. and J. B. Young Co., 1900).

surface. If  $\sigma$  is the total area of the surface then the work  $dw$  needed to increase the total area by an amount  $d\sigma$  is obviously

$$dw = \gamma d\sigma \quad (19.1)$$

Now this process is supposed to take place at constant temperature and pressure, so that this work causes a change not in the total energy, but in the free energy. Hence we may write for such a process

$$dF = \gamma d\sigma \quad (19.2)$$

The surface tension may therefore be defined as

$$= \left( \frac{\partial F}{\partial \sigma} \right)_{T, P} \quad (19.3)$$

and the general equation for the change in  $F$  caused by variations in temperature, pressure, and surface area becomes

$$dF = -SdT + VdP + \gamma d\sigma \quad (19.4)$$

Since  $dF$  must be a perfect differential, it follows that

$$-\left( \frac{\partial S}{\partial \sigma} \right)_{T, P} = \left( \frac{\partial \gamma}{\partial T} \right)_{P, \sigma} \quad (19.5)$$

The fact that  $\gamma$  is independent of  $\sigma$  allows Equations (19.2) and (19.5) to be integrated at once. Integrating (19.2) gives

$$F = F_0 + \gamma\sigma \quad (19.6)$$

where  $F_0$  is readily interpreted as the ordinary free energy with surface tension neglected. In the same way

$$S = S_0 - \left( \frac{\partial \gamma}{\partial T} \right)_{P, \sigma} \sigma \quad (19.7)$$

with  $S_0$  the ordinary entropy. From these equations we find for the energy

$$E = E_0 + \sigma \left[ \gamma - \left( \frac{\partial \gamma}{\partial T} \right)_{P, \sigma} T \right] \quad (19.8)$$

We conclude therefore that the surface tension increases the free energy (and also the work function  $A$ ) by an amount  $F_\sigma = \gamma\sigma$ , the entropy by an amount  $S_\sigma = -\sigma \left( \frac{\partial \gamma}{\partial T} \right)_{P, \sigma}$ , and the energy by an amount  $E_\sigma = \sigma \left[ \gamma - \left( \frac{\partial \gamma}{\partial T} \right)_{P, \sigma} T \right]$ .

These results enable us to calculate the heat effects which accompany a change in the surface area of a liquid. If the surface is increased isothermally by an amount  $\Delta\sigma$ , the heat absorbed is  $T\Delta S = -\left( \frac{\partial \gamma}{\partial T} \right)_{P, \sigma} \Delta\sigma$ . As we shall see later,  $\left( \frac{\partial \gamma}{\partial T} \right)_{P, \sigma}$  is always negative, so that the heat absorbed is positive.

(20) **The Origin of Surface Tension:** Surface tension must have its origin in the attractive forces between molecules which hold the liquid together. As we have already seen, these forces act over very short ranges, and to a first approximation may be considered to act only between nearest neighbors. A molecule in the interior of the liquid is completely surrounded by neighboring molecules, and is attracted by each one. It has therefore a low potential energy. A molecule on the surface, on the other hand, has only approximately half as many nearest neighbors, so that its binding energy is only about half as great as that of an interior molecule. It follows that the energy of a surface molecule is greater than that of an interior molecule by some quantity, say  $\epsilon$ . If we now consider the total energy of the liquid, this will not be simply the average energy per interior molecule times the number of molecules, but this quantity plus an additional energy proportional to  $\epsilon$  and to the number of surface molecules, which in turn is proportional to the surface area.

In the same way the molecules in the surface of a liquid must be expected to have a preferential orientation with respect to the surface. This orientation effect alone would be expected to decrease the entropy of the liquid. But, in addition, there is the disordering effect of the greater freedom of motion of the surface molecules which tends to increase the entropy. The net effect of these opposing tendencies always seems to be such that the entropy of the surface is positive, i.e., the disorder created by the increased freedom of motion is greater than the ordering effect of the surface.

We see then that the surface free energy is the sum of a positive energy term and a negative entropy term. At low temperatures the energy term predominates: the surface free energy, and hence the surface tension is positive. As the temperature increases the contribution of the entropy term becomes larger, being multiplied by  $T$  in the free energy, and the surface tension decreases. At a sufficiently high temperature, in the neighborhood of the critical point, the surface tension becomes zero.

(21) **The Pressure Drop across a Curved Surface:** The measurement of surface tension by most of the common methods depends on the fact that the

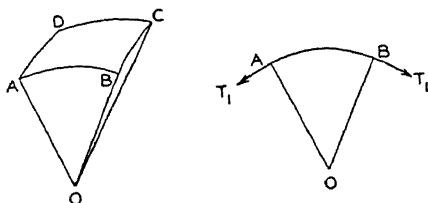


FIG. 13. Calculation of Pressure Drop across Curved Surface.

surface tension tends to flatten out any curvature in a surface. This flattening effect will generally be opposed by a difference of pressure between the two sides of the surface, which at equilibrium exactly balances the tendency of the surface to contract.

The amount of this pressure difference is easily found. Consider an infinitesimal surface element formed by a rectangle whose sides are parallel to the principal circles of curvature in the surface (Fig. 13). The surface tension acting along the side  $AD$  is  $T_1 = \gamma AD$ , while an equal force acts along  $BC$ . If  $O$  is the center of curvature of  $AB$ ,  $R_1$  its radius of curvature, and  $\theta_1$  the angle

subtended at  $O$  by  $AB$ , the vector sum of the two tensions is  $2T_1 \sin \frac{1}{2}\theta_1$ , or since  $\theta_1$  is small,  $T_1\theta_1 = \gamma\theta_1 AD$ . In the same way the resultant force of the tensions acting along  $AB$  and  $CD$  is  $\gamma\theta_2 AD$ , where  $\theta_2$  is the angle subtended by  $AD$  at its center of curvature. The total force on the surface element in the direction normal to the surface is therefore

$$\gamma\theta_1 AD + \gamma\theta_2 AD$$

Since the area of the surface element is  $AB \times AD$  the resultant pressure is

$$P = \gamma \left( \frac{\theta_1}{AB} + \frac{\theta_2}{AD} \right) \quad (21.1)$$

or, if  $R_1$  is the radius of curvature of  $AB$  and  $R_2$  that of  $AD$

$$P = \gamma \left( \frac{1}{R_1} + \frac{1}{R_2} \right) \quad (21.2)$$

Hence the pressure is higher on the concave side of the surface by an amount proportional to the surface tension.

If the pressure is equal on the two sides of the surface,  $1/R_1 + 1/R_2$  must vanish, or  $R_1 = -R_2$ . It has been shown by Plateau that this condition is accurately obeyed in the case of soap films.<sup>1</sup>

(22) **Capillarity:** Along a line at which the surface between two liquids meets a solid surface the tensions existing in the three boundaries must be in equilibrium. This is generally possible if the boundary between the two fluids makes a definite angle with the solid surface, the contact angle. In the case where one of the fluids involved is a gas and the other a liquid, the contact angle is usually defined as the angle between the liquid-gas surface and the liquid-solid surface. In many cases, such as water against glass, the contact angle is zero; while in others, such as mercury against glass, the contact angle may rise as high as  $180^\circ$ .

If a liquid is placed inside a solid tube, the requirement that the liquid-gas interface must meet the liquid-solid interface at the correct contact angle prevents the surface of the liquid from being plane. The resulting curvature of the surface creates the pressure difference of the previous section, which in turn forces the surface to move toward its concave side. Thus water will tend to move into a glass tube, while mercury will tend to move out of such a tube.

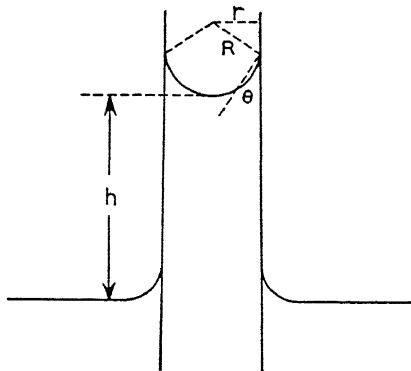


FIG. 14. Capillary Rise.

<sup>1</sup> J. Plateau, *Statique expérimentale et théorique des liquides soumis aux seules forces moléculaires* (Paris: Gautier-Villars et Cie, 1873).

If the tube is vertical, the pressure difference due to the effect of gravity will sooner or later balance that caused by surface tension, and the capillary action of the tube will be brought to an end after a definite rise or fall of the liquid in the tube. Let the height to which the liquid rises in the tube be  $h$  (Fig. 14), the density of the liquid be  $\rho$  and the density of the surrounding gas be  $\rho'$ . If  $P_0$  is the pressure at the free surface of the liquid outside the capillary, then at the bottom of the meniscus the pressure must be  $P_0 - \rho'gh$  for the gas around the liquid to be in equilibrium. Inside the liquid, on the other hand, the pressure is  $P_0 - \rho gh$ . The pressure drop across the surface is therefore  $(\rho - \rho')gh$ . This must be equal to that of Equation (21.2), so that at equilibrium

$$(\rho - \rho')gh = \gamma \left( \frac{1}{R_1} + \frac{1}{R_2} \right) \quad (22.1)$$

If the tube has the form of a cylinder of revolution the two radii of curvature are equal at the bottom of the meniscus and we may write

$$h = \frac{2\gamma}{(\rho - \rho')gR} \quad (22.2)$$

In general the radius of curvature  $R$  is greater than  $r$ , the radius of the tube. If the tube is narrow, however, it has been shown<sup>1</sup> that the surface of the liquid is very nearly spherical. In this case it is easily seen from Fig. 14 that  $R = r/\cos \theta$  where  $\theta$  is the contact angle. Hence

$$h = \frac{2\gamma \cos \theta}{g(\rho - \rho')r} \quad (22.3)$$

In very accurate work correction must be made for the non-sphericity of the meniscus. It has been shown by Rayleigh<sup>2</sup> that, for narrow tubes,

$$R = r \left( 1 + \frac{1}{3} \frac{r}{h} - 0.1288 \frac{r^2}{h^2} + 0.1312 \frac{r^3}{h^3} \dots \right) \quad (22.4)$$

For an extensive account of the necessary corrections the reader is referred to Adam.<sup>1</sup>

(23) **Bubble Pressure:** The pressure inside a soap bubble is given immediately by Equation (21.2). If  $P_0$  is the pressure inside the bubble, the pressure within the film is (assuming the bubble to be a sphere of radius  $R$ )

$$P_0 + \frac{2\gamma}{R} \quad (23.1)$$

On passing from the interior of the film to the gas within the bubble there is a second pressure increase due to the inner surface, so that the pressure difference

<sup>1</sup> N. K. Adam, *Physics and Chemistry of Surfaces* (New York: Oxford University Press, 1930), p. 295.

<sup>2</sup> Rayleigh, *Proc. Roy. Soc.*, A92, 184 (1915).

between the gas inside the bubble and the gas outside is

$$\Delta P = 4\gamma/R \quad (23.2)$$

If a capillary tube is immersed in a liquid and the gas pressure inside the tube is increased, bubbles will be formed at the bottom of the tube. If we assume that these bubbles are spherical, the pressure inside the tube will be equal to the hydrostatic pressure at the bottom of the tube,  $gh(\rho - \rho')$ , where  $\rho$  and  $\rho'$  are again the densities of the liquid and gas, plus the pressure difference due to the surface tension,  $2\gamma/R$ . As the size of the bubble increases  $R$  first decreases until the bubble is a hemisphere and  $R$  is equal to the radius  $r$  of the tube. If the bubble is enlarged further, the radius of the bubble once more increases. The pressure is therefore a maximum when the bubble is hemispherical, the maximum pressure being equal to

$$gh(\rho - \rho') + \frac{2\gamma}{r}$$

Since the pressure decreases as the bubble increases in size beyond this point, the bubble so formed is unstable, and will break off the end of the tube.

Measurement of this maximum bubble pressure has frequently been used to measure surface tension, and with proper precautions and corrections for the departure of the shape of the bubble from the spherical is capable of precise results.

(24) **Drop Formation:** When a drop of liquid is formed at the end of a capillary tube, the weight of the drop is supported by the surface tension. When this weight becomes too large the drop falls. If  $r$  is the radius of the tip, and  $\theta$  is the angle made by the liquid surface with the vertical at the line where it meets the tip, the total upward force due to surface tension is

$$2\pi r\gamma \cos \theta$$

This is the maximum drop weight which can be supported by the tip.

This relationship is the basis for an important method of measuring surface tension. The method consists, however, of a determination of the weight of the drop which *falls* from the tip, and unfortunately this is not equal to the weight suspended at the tip, for only a part of the drop falls. The relationship between the weight of the falling drop and the weight of the suspended drop has been the subject of much careful study, particularly by Lohnstein,<sup>1</sup> and by Harkins and Brown.<sup>2</sup> It is found that the fraction of the suspended drop which falls is a function  $f(r/R)$  where  $R$  is the radius of the falling drop. Since  $\theta$  ordinarily seems to be 0, the weight of the falling drop is

$$W = 2\pi r\gamma f(r/R) \quad (24.1)$$

Values of  $f(r/R)$  for various radius ratios are given in Table VIII. In a meas-

<sup>1</sup> Lohnstein, *Ann. Physik*, 20, 237, 606 (1905); *ibid.*, 21, 1030 (1906); *ibid.*, 22, 767 (1907).

<sup>2</sup> Harkins and Brown, *J. Am. Chem. Soc.*, 41, 499 (1919).



urement of surface tension the mass of a falling drop is found, and from this and the density of the liquid, the radius of the drop. Table VIII may then be used to find the fraction of the suspended drop which fell, and hence the mass of the suspended drop. Equation (24.1) then gives the surface tension.

TABLE VIII

$R/r$	$f$	$R/r$	$f$
17.10	0.925	0.6787	0.60070
3.864	0.804	0.6612	0.60270
2.403	0.740	0.6450	0.6047
1.8042	0.7055	0.6301	0.6082
1.6168	0.6905	0.6162	0.6117
1.4690	0.67662	0.6016	0.6157
1.3494	0.66381	0.5911	0.6193
1.2504	0.65233	0.5797	0.6241
1.1672	0.64212	0.5689	0.6281
1.0964	0.63320	0.5583	0.6323
1.0357	0.62613	0.5487	0.6369
0.9827	0.62022	0.5396	0.6412
0.9358	0.61512	0.5306	0.6459
0.8942	0.61061	0.5223	0.6509
0.8570	0.60691	0.5144	0.6550
0.8238	0.60400	0.5055	0.6550
0.7935	0.60167	0.4962	0.6520
0.7662	0.60009	0.4867	0.6470
0.7413	0.59918	0.4771	0.6389
0.7186	0.59909	0.4675	0.6301
0.6978	0.59959	0.4582	0.6219

(25) **The Tensiometer:** A very convenient method of measuring surface tension is to measure the force necessary to detach a wire ring from the surface of the liquid. The tensiometer devised by du Noüy<sup>1</sup> is based on this principle. In it the force needed to pull a platinum ring from the surface is measured by means of a torsion wire.

As the ring is lifted from the surface, a film of liquid is pulled up with it. If the constricted surface of the film becomes vertical before it breaks, the downward force due to surface tension at the constriction is twice the product of the circumference of the ring and the surface tension. This force is balanced by the upward force on the ring, less the weight of the ring and that of the liquid above the vertical portion of the film. If the weight of the ring is compensated and the weight of this liquid is neglected, the upward pull on the ring necessary to maintain equilibrium is given by

$$F = 4\pi R\gamma \quad (25.1)$$

where  $R$  is the radius of the ring.

<sup>1</sup> du Noüy, *J. Gen. Physiol.*, 1, 521 (1919).

To obtain accurate measurements of the surface tension it is necessary to modify Equation (25.1) to allow for the weight of the liquid raised above the vertical portion of the film, and also for the fact that the film may not become vertical before breaking. These corrections depend on both the radius of the ring and the radius of the wire from which it is made. The method has been studied carefully by Harkins and his coworkers.<sup>2</sup> They find that the surface tension can be found accurately from the equation

$$\gamma = \frac{\star}{4\pi R} f \quad (25.2)$$

where  $f$  is a function of the variables  $R^3/V$  and  $R/r$ ,  $V$  is the volume of liquid raised, and  $r$  is the radius of the wire. By using the factor  $f$ , which varies from 1.1 to 0.75, the results compare with those obtained by the most accurate methods.<sup>3</sup>

<sup>2</sup> Harkins, Young, and Chang, *Science*, **64**, 333 (1926); Harkins and Young, *International Critical Tables*, **4**, 432; Harkins and Jordan, *6th Colloid Symposium Monograph*, 39 (1928).

<sup>3</sup> For a further treatment of surface tension, see this volume, p. 568, *et seq.*



## CHAPTER IV

### X-RAY ANALYSIS OF THE SOLID STATE

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#### CRYSTAL GEOMETRY

(1) **The Nature of Real Crystals:** Crystals differ from amorphous substances in properties which are essentially directional. The plane face boundaries, which were once a criterion of crystallinity, show that growth itself has occurred at varying rates in different directions. Although the relative development of different faces may vary for crystals of a given substance grown under different conditions, the angles between the faces are constant, and when a crystal is broken it cleaves along definite planes to give smaller crystals. Absorption and refraction of light are anisotropic, i.e., they depend on the orientation of the crystal. Some crystals show piezo- and pyro-electric effects differentiating one side of the crystal from the opposite side.

The macroscopic properties of crystals can only be explained satisfactorily by a sub-microscopic regularity of the building units of the crystals. This view was put forward by Häuy in 1822<sup>1</sup> and from that time the science of crystallography began to develop the theoretical geometrical framework which is necessary in the present-day detailed structure analyses of crystals by X-ray diffraction.

One consequence of the new knowledge of the solid state gained in recent years has been a broadening of the term crystalline to include substances which have an ordered fine structure in one, two or three dimensions, whether or not they exhibit all the macroscopic properties previously associated with crystals. For example, many so-called amorphous substances are shown to consist of aggregates of very small single crystals. Fibers in general have an ordered structure in one direction, along the fiber axis, but a random arrangement perpendicular to this axis. Such substances are crystalline in one dimension.

(2) **The Three-dimensional Lattice:** A three-dimensional lattice is derived by repetition of a unit of pattern by translations along three lattice directions or axes. Hence the lattice can be represented by a set of vectors and as such has no unique origin. In crystallographic problems an origin may be taken, for example, to coincide with a symmetry center, in order to simplify calculations, but this is not fundamental. The parallelepiped formed by translations along the three lattice axis is called the unit cell.

<sup>1</sup> *Traité de Cristallographie*, Paris (1822).

Figure 1 shows in two dimensions that for a given lattice alternative axes can be chosen and therefore alternative unit cells. The cell formed by the vectors  $a$ ,  $b$  contains one unit of pattern and is termed primitive, while that formed by  $a$ ,  $b'$  contains two units of pattern and is doubly primitive. Multiply primitive cells are referred to as face-centered, body-centered or end-centered according to Fig. 2. It is possible, of course, to choose a primitive cell for any lattice but in certain cases multiply primitive cells are more convenient.

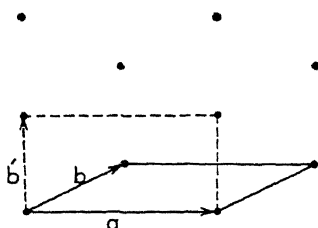


FIG. 1.

If a lattice plane makes intercepts with the  $a$ ,  $b$  and  $c$  axes  $\frac{a}{h}$ ,  $\frac{b}{k}$ ,  $\frac{c}{l}$  respectively, then the equation of the plane is

$$x \left/ \frac{a}{h} \right. + y \left/ \frac{b}{k} \right. + z \left/ \frac{c}{l} \right. = 1$$

or

$$\frac{hx}{a} + \frac{ky}{b} + \frac{lz}{c} = 1 \quad (2.1)$$

The coefficients  $h$ ,  $k$ ,  $l$ , which are the reciprocals of the axial intercepts of the plane, are termed the Miller indices of the plane and are sufficient to specify the plane completely. In order to transform the indices of a plane from those

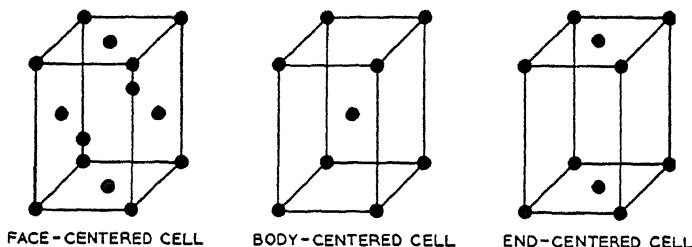


FIG. 2.

corresponding to cell axes  $a$ ,  $b$ ,  $c$  to new indices corresponding to cell axes  $A$ ,  $B$ ,  $C$  it is necessary to use the vectorial relations between the old axes and the new. This is illustrated in two dimensions in Fig. 3, where  $a$ ,  $b$  and  $A$ ,  $B$  are two sets of axes.

Now

$$A = 2a + b \quad (2.2)$$

$$B = a + 2b \quad (2.3)$$

In the general case

$$A = u_1a + v_1b + w_1c \quad (2.4)$$

$$B = u_2a + v_2b + w_2c \quad (2.5)$$

$$C = u_3a + v_3b + w_3c \quad (2.6)$$

Equations (2.4) to (2.6) are expressed most concisely by the matrix of transformation of axes

$$\begin{pmatrix} u_1 & v_1 & w_1 \\ u_2 & v_2 & w_2 \\ u_3 & v_3 & w_3 \end{pmatrix} \quad (2.7)$$

Now as a change is made in the axes of reference a change is also made in the intercepts which a given plane will make with these axes. The reciprocals of the axial intercepts will vary according to exactly the same relations as the axes themselves; hence the new indices of the plane are obtained from the old by direct use of the matrix (2.7).

The law of rational indices of classical crystallography states that the Miller indices of crystal faces are small integers. In practice an index greater than 5 never occurs. From the above discussion of the three-dimensional lattice it is clear that a plane of small indices will be much more densely packed with lattice

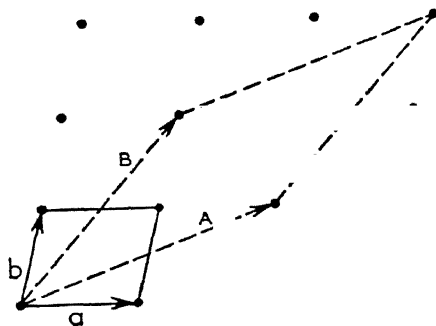


FIG. 3.

points than a plane with large indices, and it is logical, therefore, on a purely geometrical basis, that high indices are not likely to be observed for actual crystal faces. However, this is only one factor in face development, for the simplest planes are not necessarily those which are most highly developed, e.g.,  $20\bar{1}$  may be observed while  $001$  is not. The simple Bravais law, that the most densely packed planes will occur as crystal faces, was extended by Donnay and Harker<sup>1,2</sup> to take into account the effect of symmetry operations on the meaning of Miller indices and some success was achieved in explaining crystal morphology,<sup>3</sup> but anomalies still exist.

The lattice of a crystal is not simply a geometrical array of points but a pattern of atoms and molecules which contain anisotropic electric forces. Gibbs<sup>4</sup> considers that the condition for a crystal to exist in equilibrium with its

<sup>1</sup> *Compt. rend.*, 204, 274 (1937).

<sup>2</sup> *Amer. Mineral.*, 22, 446 (1937).

<sup>3</sup> *Amer. Mineral.*, 23, 5 (1938); *ibid.*, 24, 184 (1939).

<sup>4</sup> Gibbs, *Collected Works*, Vol. I (New York: Longmans, Green & Co., 1931), p. 320.

surroundings is that its total free energy for a given volume is a minimum, i.e.,

$$\sum A_i g_i \quad \text{minimum} \quad (2.8)$$

where  $g_i$  is the surface free energy per unit area of the  $i$ th face of area  $A_i$  on a crystal bounded by  $N$  faces. As Gibbs pointed out, this relation could only apply to very small crystals in equilibrium with the solution. Even this may be an over simplification of the problem, and in any case the relation is very

difficult to verify experimentally. A comprehensive review of the subject of crystal growth has been given by Wells.<sup>5</sup>

### (3) Macroscopic Symmetry:

Although exact crystal shapes may vary with conditions of growth the constancy of interfacial angles provides a basis for the construction of an "ideal crystal" the occurrence and disposition of the faces of which indicate the crystal symmetry. A symmetry operation is one which will bring the crystal

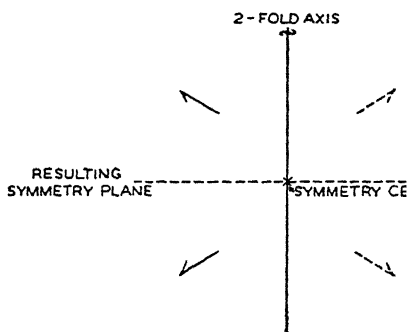


Fig. 4.

into self-coincidence. A crystal with no symmetry at all is designated by a one-fold rotation axis of symmetry as any body is unchanged by a rotation of  $360^\circ$ . The possible symmetry elements are:

- (1) A center of symmetry or center of inversion. This is a point within the crystal such that every point in the crystal has an equivalent point on the line joining it to the center of symmetry and an equal and opposite distance from the center.
- (2) Axes of symmetry, which may be two-, three-, four-, or six-fold rotation axes. In general an  $n$ -fold rotation axis of symmetry will bring the crystal into self-coincidence by a rotation of  $360^\circ/n$ .
- (3) Axes of rotatory inversion are two-, three-, four-, or six-fold rotation axes combined with a center of inversion.
- (4) A plane of symmetry will give self-coincidence by reflection perpendicular to the plane. A two-fold rotation axis combined with a center of symmetry gives rise to a reflection plane as illustrated in Fig. 4. The resulting plane of symmetry is horizontal and perpendicular to the plane of the paper.

Figure 5 illustrates the symmetry elements of a regular tetrahedron. There are three twofold rotation axes and six planes of symmetry but no center of

<sup>5</sup> *Chem. Soc., (London) Annual Reports*, 43, 62 (1946).

inversion. The nomenclature of crystal symmetry elements can be summarized as follows:

- center of symmetry  $\bar{1}$   
 $n$ -fold rotation axis of symmetry,  $n$  ( $n = 2, 3, 4$  or  $6$ )  
 $n$ -fold axis of rotatory inversion,  $\bar{n}$  ( $\bar{n} = 2, 3, 4$  or  $6$ )  
 Plane of symmetry,  $m$ .

It can be shown that there are 32 possible combinations of these symmetry elements giving the 32 crystal classes. Combinations of symmetry elements frequently give rise to further symmetry elements as shown in Fig. 4 above. For simplicity, therefore, only those elements which are necessary to specify the crystal class are used, any additional elements which are produced by the given operations being omitted. The first symbol refers to the principal symmetry axis e.g., 2, 3 or  $\bar{4}$ . A plane of symmetry perpendicular to the principal axis is written  $2/m$ ,  $4/m$  etc.; where there is no stroke between the two symbols the symmetry plane is parallel to the axis, not perpendicular. Finally the symbols for secondary symmetry axes are given where these occur. Such a set of symmetry elements describing a single crystal is termed a point group to distinguish it from a space group, the set of symmetry elements describing a lattice.

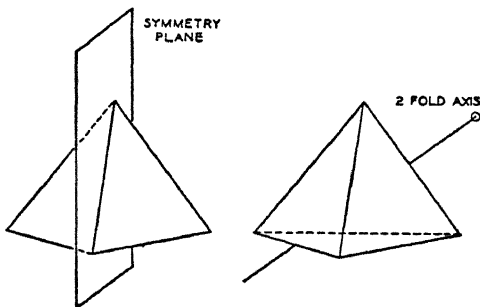


FIG. 5.

On the basis of type of unit cell crystals are divided into seven systems.

- (1) Triclinic. There are three unequal axes making unequal angles (not  $90^\circ$ ) with each other. The only possible symmetry element is a center of inversion, therefore the only triclinic classes are 1 and  $\bar{1}$ .
- (2) Monoclinic. The three axes are unequal and one axis,  $b$ , is at right angles to the other two which make an angle  $\beta$ , not  $90^\circ$ . The crystal classes are 2,  $\bar{2}$  and  $2/m$ .
- (3) Orthorhombic. The axes are unequal and all at right angles. The crystal classes of the orthorhombic system are  $2m$ ,  $22$  and  $2/mmm$ .
- (4) Trigonal. Three equal axes make equal angles (not  $90^\circ$ ) with each other. The classes all include a threefold axis, viz., 3,  $\bar{3}$ ,  $3m$ ,  $\bar{3}m$ ,  $32$ .
- (5) Tetragonal. Two of the axes are equal and all three are at right angles. The crystal classes are 4,  $\bar{4}$ ,  $4/m$ ,  $4m$ ,  $\bar{4}m$ ,  $42$  and  $4/mmm$ .
- (6) Hexagonal. There are three equal axes in the same plane at  $120^\circ$ . It is customary to choose any two of these as  $a$  and  $b$  while  $c$  is unequal and perpendicular to  $a$  and  $b$ . The hexagonal crystal classes are 6,  $\bar{6}$ ,  $6/m$ ,  $6m$ ,  $\bar{6}m$ ,  $62$  and  $6/mmm$ .



- (7) Cubic. The three axes are equal and at right angles. The five cubic classes are  $23$ ,  $2/m3$ ,  $\bar{4}3m$ ,  $432$ ,  $m3m$ .

(4) **Lattice Symmetry:** In a three-dimensional lattice there are symmetry operations which cannot appear in point group symmetry. With a single crystal, repeated operation of a symmetry element always brings a point in the crystal back to exactly the same position, but in a lattice there are additional possible symmetry elements repeated operation of which will bring a lattice point into coincidence with a neighboring lattice point. These are the glide plane and the screw axis. The glide plane is shown in Fig. 6. The unit of

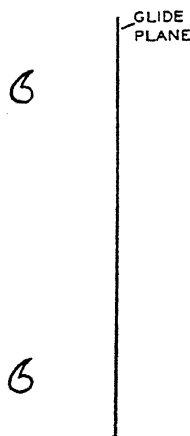


FIG. 6.

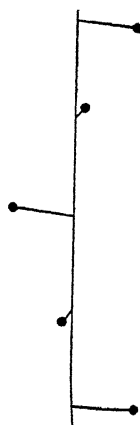


FIG. 7.

pattern is reflected across the glide plane, which is perpendicular to the plane of the paper, and is then translated parallel to the plane. There are three types of glide plane (1) axial glide, parallel to a cell axis with translation  $a/2$ ,  $b/2$  or  $c/2$  designated  $a$ ,  $b$  or  $c$ ; (2) diagonal glide, parallel to a cell diagonal with translation  $a/2 + b/2$ ,  $b/2 + c/2$  or  $a/2 + c/2$ , designated  $n$ ; and (3) diamond glide, parallel to a cell diagonal in certain multiply primitive cells, with translation  $a/4 + b/4$ ,  $b/4 + c/4$  or  $a/4 + c/4$ , designated  $d$ . A screw axis is a simple rotation axis combined with a translation down the axis as shown in Fig. 7. Screw axes are designated  $N_m$  where the rotation is  $360^\circ/N$  and the translation  $m/N$  of the axial periodicity. Thus  $6_1$  represents a rotation of  $60^\circ$  and a translation of  $1/6$  of the axis. Conventionally, screw axes are named in terms of a right-handed screw.

In a three-dimensional lattice, with the addition of the glide plane and screw axis to the symmetry elements previously described, it is possible to reproduce the unit of pattern in 230 different ways giving the 230 space groups.<sup>1</sup>

<sup>1</sup> For space group theory see Hilton, *Mathematical Crystallography and the Theory of Space Groups of Movements* (New York: Oxford University Press, 1903). The 230 space groups are described in *Internationale Tabellen zur Bestimmung von Kristallstrukturen* (1935).

The 32 crystal classes are simply the space groups without the special properties of glide planes and screw axes. Five-fold and more than six-fold axes of symmetry do not occur in crystals because they are incompatible with the existence of a continued lattice, which is the fine structure of crystals. The naming of space groups follows the same system used for point groups with the additional symmetry symbols. The type of unit cell is shown by the first letter, *P* for a primitive cell, *F* for face-centered, *A*, *B* or *C* for a cell centered on the *a*, *b* or *c* face and *I* for a body-centered cell. Thus the monoclinic space group  $P2_1/c$  means a primitive unit cell with the principal axis a twofold screw axis and perpendicular to it a glide plane with translation  $c/2$ . The operations of this space group are shown diagrammatically in Fig. 8, which gives two projections

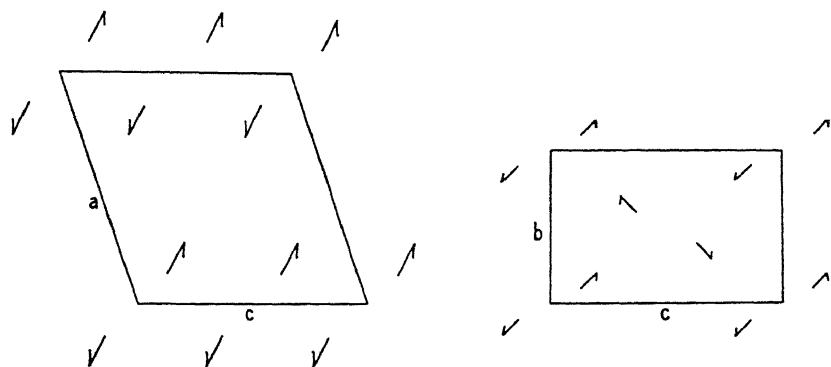


FIG. 8.

of a hypothetical structure. The asymmetric unit is reproduced four times within the unit cell, and the equivalent points are readily seen to be

$$\pm (x, y, z); (x, y + \frac{1}{2}, \frac{1}{2} - z) \quad (4.1)$$

A center of symmetry is produced at the origin and at  $(0, \frac{1}{2}, \frac{1}{2})$  by the combination of the other symmetry elements.

(5) **Crystal Representation:** In describing geometrical properties of crystals it is convenient to employ graphical methods in order to represent all crystal planes in two dimensions. The two principal methods employed in classical crystallography are stereographic and gnomonic projections. In stereographic projections a sphere is first constructed around the crystal. The points on the sphere which intersect the normals to the crystal planes from the center are the poles of the planes and if the poles are then projected on to a selected plane a complete representation of the crystal planes is obtained. A gnomonic projection is made by taking the points at which normals to the crystal planes from a fixed point within the crystal meet a given plane. The disadvantage of the gnomonic projection is that planes perpendicular to the projection plane are not represented in the projection but stereographic and gnomonic projections are sometimes used together in the same diagram.



in this research that an experiment designed to establish the wave nature of X-rays gave rise to the new science of X-ray crystallography. X-rays could be characterized by their properties of ionizing gases, exciting fluorescence in certain materials and blackening photographic plates. The radiation was not deflected by magnetic fields and hence could not be a stream of charged particles. If X-rays were electromagnetic waves, similar to ordinary light but of shorter wavelength, then they should have the properties of diffraction, refraction and polarization.

The first diffraction experiments were carried out by Haga and Wind<sup>1</sup> who passed a beam of X-rays through a very narrow slit and observed a broadening of the band. Later workers carried out more refined experiments and the measurements gave a value of  $10^{-8}$  to  $10^{-9}$  cm for the short wavelength or "hard" X-rays. Now this range is of the same order of magnitude as the interatomic distances in crystals as calculated from physical properties and Avogadro's Number, and von Laue, in 1912, suggested the use of a crystal to form interference maxima with X-rays. Refraction of X-rays was not observed by early workers as the measurable effect is very small, but was established by Duane and Patterson<sup>2</sup> by use of a calcite crystal. Polarization of X-rays should, according to electromagnetic theory, occur when the radiation is scattered at an angle of  $90^\circ$  and this effect was observed qualitatively by Barkla<sup>3</sup> in 1906 by scattering from blocks of carbon. These experiments have been put on a quantitative basis by Compton and Hagenow<sup>4</sup> who by correcting for various errors showed that the scattered rays were completely polarized as predicted by the theory.

The wavelength of X-rays is characteristic of the target used and of the accelerating potential of the bombarding electrons. The spectrum produced consists of very sharp maxima when a critical range of voltage is used and these are related in frequency to the material of the target. In addition there is a continuous spectrum known as white radiation which extends to a limit on the short wave side given by the equation

$$Ve = h\nu \quad (6.1)$$

where  $V$  is the accelerating potential,  $e$  the electronic charge,  $h$  Planck's constant and  $\nu$  the limiting frequency. If the potential used is not sufficient to excite the characteristic radiation of the target element, then the spectrum is almost entirely the continuous spectrum. In crystallographic work it is normally desirable to use X-rays of one wavelength and optimum voltages are used to give the best intensity of the required band.

The absorption of X-rays depends on the wavelength and also on the absorbing material. If  $dI/I$  is the fraction of the intensity of a beam of X-rays

<sup>1</sup> *Wied. Ann.*, **68**, 884 (1899).

<sup>2</sup> Duane and Patterson, *Phys. Rev.*, **16**, 526 (1920).

<sup>3</sup> *Phil. Trans. Roy. Soc. (London)*, **204**, 467 (1905).

<sup>4</sup> *J. Opt. Soc. Am. and Rev. Sci. Inst.*, **487** (1924).

of intensity  $I$  absorbed by a thickness  $t$  of material then

$$dI/I = -\mu dx$$

and

$$I = I_0 e^{-\mu t} \quad (6.2)$$

$I_0$  is the original intensity of the beam and  $I$  the intensity after passing through a thickness  $t$  of absorbing material.  $\mu$  is the absorption coefficient of the absorbing material for the particular wavelength used but it is more convenient

to use a "mass absorption coefficient"  $\mu/\rho$  where  $\rho$  is the density of the substance, as this coefficient is almost independent of physical state. The absorption of an element does not vary significantly in different states of chemical combination; hence, it is possible to calculate the absorption of any compound from a knowledge of the "atomic absorption coefficients" for a given wavelength, and the density. Absorption of X-rays of a given wavelength does not increase indefinitely with increase in atomic number of the absorber. There is an increase in absorption up to a certain critical value at which point there is an abrupt drop. Such a discontinuity is called an "absorption edge" and is illustrated for  $\text{Cu}K_\alpha$  in Fig. 10. This property is used in filtering characteristic X-radiation. The most important spectral components are  $K_{\alpha_1}$ ,  $K_{\alpha_2}$

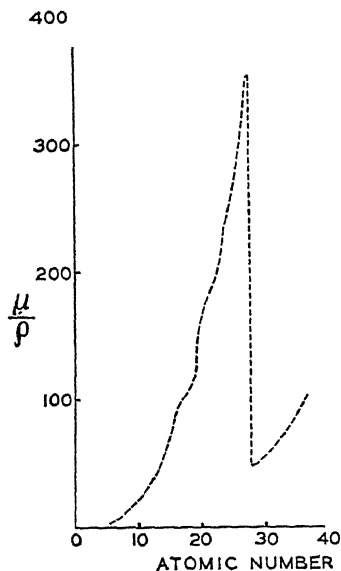


FIG. 10.

and  $K_{\beta_1}$ .  $K_{\alpha_1}$  and  $K_{\alpha_2}$  are a very close doublet only resolved at high angle scattering. The  $\beta_1$  ray has a rather shorter wavelength and it is possible to find a filter, an absorption edge of which comes between the  $\alpha$  and  $\beta_1$  components thus removing most of the  $\beta_1$  but remaining transparent to the  $\alpha_1\alpha_2$  doublet. A thin piece of nickel foil will screen off most of the  $K_{\beta_1}$  in the characteristic copper radiation.

(7) **Diffraction of X-rays by Crystals:** X-rays are scattered by electrons by setting them into forced vibrations. The electron is accelerated and decelerated and, as it is oscillating in phase with the primary beam, produces a "scattered" beam of the same wave length. Von Laue's original experiment<sup>1</sup> was based on the assumptions that a crystal has a periodic distribution of electrons in three dimensions and that interatomic distances are of about the same magnitude as the wavelength of X-rays. On this basis the scattered rays

<sup>1</sup> W. Friedrich, P. Knipping and M. Laue, *Ber. Bayer. Akad. Wiss.*, 303 (1912).

should cooperate in certain definite directions where they are in phase. This was found to be the case but the first mathematical treatment employed is not the simplest.

Figure 11 shows in the one dimensional case the scattering of X-rays by a regular row of particles  $a$  units apart.  $\varphi$  is the angle between the row and the incident wave front,  $AC$ , and  $\alpha$  the angle between the row and the diffracted wave front,  $BD$ . For the beams scattered by the atoms  $A$  and  $B$  to be in phase the path difference between the wave scattered by  $A$  and that scattered by  $B$  must be an integral number of wavelengths.

Hence

$$\begin{aligned} n\lambda &= BC - BD \\ &= a (\cos \varphi - \cos \alpha) \quad (7.1) \end{aligned}$$

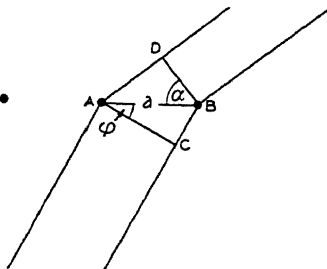


FIG. 11.

In three dimensions we have a triple set of such relations:

$$p\lambda = a (\cos \varphi_1 - \cos \alpha_1) \quad (7.2)$$

$$q\lambda = b (\cos \varphi_2 - \cos \alpha_2) \quad (7.3)$$

$$r\lambda = c (\cos \varphi_3 - \cos \alpha_3) \quad (7.4)$$

and these are the Laue relations. These expressions are not used except in the special case of the beam perpendicular to a row of points as described later in the interpretation of rotation photographs.

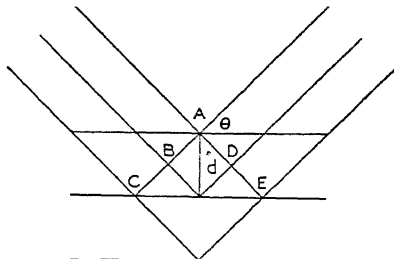


FIG. 12.

A simpler view of the problem was put forward by Bragg.<sup>2</sup> The incident beam of X-rays is regarded as being "reflected" from a series of equally spaced planes of scattering particles under the condition that the angle of incidence is equal to the angle of reflection. In Fig. 12  $ABC$  is the incident wave front,  $ADE$  the reflected wave front,  $d$  the perpendicular spacing of the planes and  $\theta$  the complement of the angle of incidence ( $\theta$  is known as the

"Bragg angle"). For the scattered waves to be in phase and cooperate the path difference  $AB + AD = 2AD$  must be equal to an integral number of wavelengths and therefore

$$n\lambda = 2d \sin \theta \quad (7.5)$$

<sup>2</sup> *Phil. Mag.*, 27, 315 (1914).

which is Bragg's law. The distribution of the particles within each plane will not affect the particular scattered beam considered. Any disorder within a plane would have most effect on reflections from planes at right angles to that plane. The Bragg law is not strictly accurate, as refraction occurs within the crystal and the angle of incidence is not exactly equal to the angle of reflection. This is not significant in crystallography but is important in determination of wavelengths and the theoretical correction has been deduced by Darwin.<sup>3</sup>

It is important to notice the difference between diffraction of monochromatic X-rays by a crystal and the corresponding diffraction grating effect for monochromatic light. With the grating all orders of reflection are present simultaneously while in crystal diffraction the reflected beam occurs for a given set of planes only when these planes are oriented at the Bragg angle with respect to the incident beam. Thus if  $\theta$  is the angle of first order reflection, the crystal must be turned to an angle of  $\sin^{-1}(2 \sin \theta)$  for the second order to occur.

(8) **Application of Reciprocal Lattice Theory:** In the discussion of the reciprocal lattice given above the problem is considered from a purely geometrical standpoint and in Equation (5.1)  $K$  is an arbitrary constant. When we use the reciprocal lattice in X-ray crystallographic constructions it is convenient to let  $K = \lambda$ , the wavelength of the X-rays diffracted by the crystal. Thus

$$\sigma_{hkl} = d_{hkl} \quad (8.1)$$

By combination with the Bragg equation we obtain the important relation:

$$\sigma_{hkl} = 2 \sin \theta \quad (8.2)$$

i.e., the distance of a reciprocal lattice point from the origin is equal to  $2 \sin \theta$  where  $\theta$  is the Bragg angle for the corresponding set of crystal planes. Although the reciprocal lattice geometrically has infinite extension, it is clear that for a fixed wavelength

$$\lambda \leq 2 \quad (8.3)$$

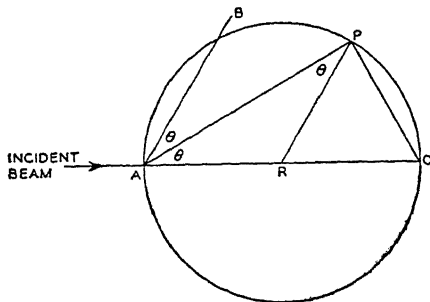


FIG. 13.

The reciprocal lattice can be considered to be bounded by a sphere of radius 2.

A geometrical representation of an X-ray reflection is shown in Fig. 13.  $P$  is a reciprocal lattice point and  $OP$  its vector.  $AP$  is the corresponding crystal plane as  $AP$  is perpendicular to  $OP$ . The incident X-ray beam passes in the direction  $Ao$ , the diameter of the circle which has radius 1.  $\angle PAR = \angle BAP = \theta$  where  $AB$  is the direction of the reflected beam and is parallel

<sup>3</sup> W. L. Bragg, *Proc. Cambridge Phil. Soc.*, 17, 43 (1913).

to  $RP$ . Since  $OP$  is constructed equal to  $2 \sin \theta$  it represents the reciprocal lattice vector in magnitude as well as direction. The condition for the occurrence of an X-ray reflection is now clear. The reciprocal lattice point lies on the surface of a sphere of radius 1 (known as the sphere of reflection) which has the end of a diameter at the reciprocal lattice origin, and the direction of reflection is parallel to the line joining the center of the limiting sphere to the reciprocal lattice point (see Fig. 14).

(9) **Intensity of the Diffracted X-ray Beam:** In the preceding sections we have been concerned with the geometrical conditions necessary for diffraction to take place and with the positions of the diffracted beams.

Both as a check on the physical theories involved, and in order to determine unknown crystal structures it is necessary to explain satisfactorily the relative intensities of the various X-ray reflections. Two cases arise, reflection from an ideal crystal and reflection from a mosaic crystal. Very few crystals are perfect. Most consist of small blocks which are not quite parallel. Intensity formulae in both cases were first given by Darwin.<sup>1</sup>

In order to make a quantitative structure determination it is necessary to relate the intensities of the X-ray reflections to the atomic positions. The structure amplitude or structure factor,  $F$ , is the ratio of the amplitude of the wave scattered by the whole unit cell to that scattered by a single electron in the same direction, under the same conditions, and it is customary to reduce the observed intensities to  $F^2$  values by various correction factors.

For a single crystal completely bathed in the incident radiation the intensities of the diffracted beams in general fall off rapidly with increase in the angle of scattering. Four factors are involved, the Lorentz factor, the polarization factor, the scattering factor and the thermal vibration of the atoms. The Lorentz factor in the rotating crystal method is a correction for the relative times throughout which different crystal planes reflect. For a zero layer, normal beam rotation photograph this is  $\frac{1}{\sin 2\theta}$  while for other layers the additional factor

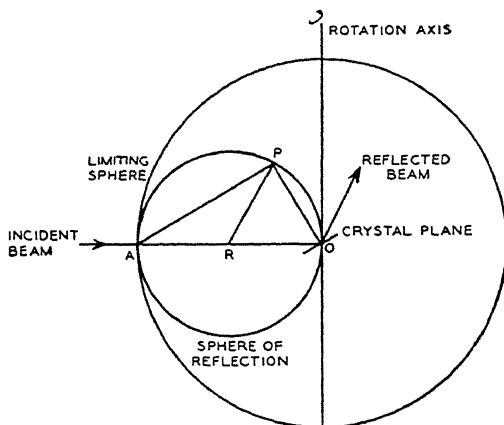


FIG. 14.

$$\cos \theta$$

<sup>1</sup> *Internationale Tabellen zur Bestimmung von Kristallstrukturen* (Berlin, 1935).



must be used where  $\theta$  is the angle between the reflecting plane and the axis of rotation. The polarization which occurs when the incident beam is reflected is allowed for by the expression  $\frac{1 + \cos^2 2\theta}{2}$ . For all rotation photographs the expression  $\frac{1 + \cos^2 2\theta}{2 \sin 2\theta}$  is required. For zero layers this is a complete correction for both the Lorentz and polarization effects and is tabulated in terms of  $\sin \theta$ .

The scattering factor allows for the falling off in intensity with increase of  $\sin \theta/\lambda$  due to the finite size of the atom. The electrons which scatter in the same atom are not all situated at a point, hence phase differences occur between the waves scattered by different electrons and the diffracted beam is weakened by varying amounts according to the angle of scattering. This factor may be regarded as the "scattering efficiency" of the atom for the Bragg angle involved.

The thermal movement of the atoms in the crystal is dependent on the crystal structure. It is considerably greater for organic compounds than for ionic crystals such as sodium chloride. The movement will have an appreciable effect on the intensity of a reflection when its magnitude becomes comparable to the distance between the reflecting planes, therefore the effect is much more marked at high angle scattering (from small spacing planes) and leads to a rapid decrease in intensity with increase in the angle of scattering. This diminution is given by

$$e^{-B(\sin \theta)^2/\lambda}$$

where

$$B = 8\pi^2 \bar{u}^2$$

$\bar{u}^2$  being the mean square amplitude of vibration of the atoms.  $B$  is a constant for each particular crystal which means that only an approximate value can be given. Further, the temperature factor is certainly anisotropic in many cases, for, particularly in organic structures, the atoms do not vibrate to the same extent in all directions and in addition even atoms of the same element may be vibrating to a varying degree. However, the effect of thermal movement of the atoms or intensities of reflections does not alter the mean positions of the atoms as obtained by the Fourier series methods described below, and it is customary to use the experimental  $F$  values corrected only for the Lorentz and polarization effects. An approximate symmetrical temperature factor is included in the scattering curve which is applied to the structure factors calculated from assumed atomic positions, and if it is desired, it is possible to refine the temperature factor as the structure itself is refined. Robertson<sup>2</sup> has given a scattering curve for anthracene which includes a large temperature factor and can be applied to many other hydrocarbon structures.

The integrated intensity of an X-ray reflection is defined by  $E\omega/I_0$  where  $E$  is the energy of the reflected beam during rotation with angular velocity  $\omega$

<sup>2</sup> *Proc. Roy. Soc.*, A150, 110 (1935).

and  $I_0$  is the energy of the incident beam per square centimeter per second. For a mosaic crystal of small volume  $dV$  completely bathed in the radiation the absolute value of the integrated intensity in terms of the structure factor can be obtained from (9.1), the measurement being assumed on a zero layer reflection.

$$\frac{E\omega}{I_0} = \left[ \frac{Ne^2}{mc^2} F(hkl) \right]^2 \lambda^3 \frac{1 + \cos^2 2\theta}{2 \sin 2\theta} dV \quad (9.1)$$

For a "perfect crystal" the expression is modified as in (9.2)

$$\frac{E\omega}{I_0} = \frac{8}{3\pi} \frac{Ne^2}{mc^2} F(hkl) \lambda^2 \frac{1 + \cos 2\theta}{2 \sin 2\theta} \quad (9.2)$$

It should be noted that for a perfect crystal  $F$  is directly proportional to the intensity while for a mosaic crystal it is proportional to the square root of the intensity. If the blocks of the crystal mosaic are too large there is a weakening of the intensities of the strongest reflections compared with the weaker. This effect is known as "primary extinction" and is the most serious source of error in evaluating the observed structure amplitudes. It can be reduced by quenching the crystal in liquid air or otherwise reducing its perfection. Secondary extinction appears as an increase in the absorption coefficient due to reflection of an appreciable part of the incident beam by the upper crystal layers before it has reached the lower layers. Ordinary absorption can be allowed for by applying the factor  $e^{-\mu t}$  to the measured intensities, where  $\mu$  is the absorption coefficient and  $t$  the mean path of the beam through the crystal. If a very small or cylindrical crystal is used this correction becomes negligible.

In order to calculate the structure factors from assumed atomic positions it is necessary to combine the waves scattered by separate atoms. This can be done by summing vectorially the amplitudes and phases of the separate scattered waves. Suppose two atoms have coordinates  $(x_1, y_1, z_1)$  and  $(x_2, y_2, z_2)$  where the cell dimensions are  $a, b$  and  $c$ . The phase differences between waves scattered by each of these atoms and a hypothetical atom at the origin are

$$2\pi \left( \frac{hx_1}{a} + \frac{ky_1}{b} + \frac{lz_1}{c} \right)$$

and

$$2\pi \left( \frac{hx_2}{a} + \frac{ky_2}{b} + \frac{lz_2}{c} \right)$$

in the reflection  $(hkl)$ . Let the scattering powers of the two atoms be  $f_1$  and  $f_2$ , respectively, thus

$$\begin{aligned} F^2 = & \left[ f_1 \cos 2\pi \left( \frac{hx_1}{a} + \frac{ky_1}{b} + \frac{lz_1}{c} \right) + f_2 \cos 2\pi \left( \frac{hx_2}{a} + \frac{ky_2}{b} + \frac{lz_2}{c} \right) \right]^2 \\ & + \left[ f_1 \sin 2\pi \left( \frac{hx_1}{a} + \frac{ky_1}{b} + \frac{lz_1}{c} \right) + f_2 \sin 2\pi \left( \frac{hx_2}{a} + \frac{ky_2}{b} + \frac{lz_2}{c} \right) \right]^2 \quad (9.3) \end{aligned}$$

This can be expressed more compactly by the use of complex quantities:

$$F = f_1 e^{2\pi i \left( \frac{hx_1}{a} + \frac{ky_1}{b} + \frac{lz_1}{c} \right)} + f_2 e^{2\pi i \left( \frac{kx_2}{a} + \frac{ky_2}{b} + \frac{lz_2}{c} \right)} \quad (9.4)$$

and, in the general case,

$$F = \sum f e^{2\pi i \left( \frac{hx}{a} + \frac{ky}{b} + \frac{lz}{c} \right)} \quad (9.5)$$

The summation is carried out over all the atoms in the unit cell. The relative scattering powers of different atoms should be directly proportional to their atomic numbers, but thermal movement is greater with lower atomic number. If the temperature factor has been included in the scattering curve atoms may be weighted at a slightly different ratio from that of their atomic numbers. If the atoms of different elements in the same structure do not differ too widely in atomic number it is possible to use a composite scattering curve. The contributions of different atoms are weighted according to an empirical ratio (e.g., oxalic acid <sup>3</sup>) and the structure factor evaluated as a fraction of the value it would have if all the atoms scattered in phase. This fraction is the geometrical structure factor ( $S$ ). Then an absolute value for the structure factor is obtained from the expression

$$F = SfZ \quad (9.6)$$

where  $f$  is the scattering factor for the reflection concerned (maximum 1) and  $Z$  is the number of electrons in the unit cell.

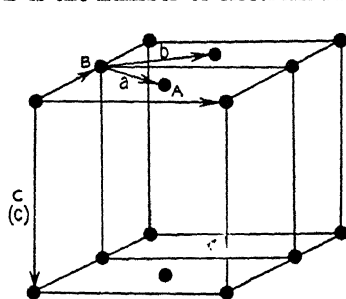


FIG. 15.

(10) **Space Group Extinction and Diffraction Symmetry:** It is not always possible to determine the space-group of a crystal uniquely from X-ray data alone, but much information is gained from extinctions or systematic absences in certain classes of X-ray reflections. The most general type of extinctions are those due to non-primitive lattices. This may be illustrated with reference to the end centered cell shown in Fig. 15.  $A$ ,  $B$  and  $C$  are the axes of the non-primitive cell which has been chosen, while  $a$ ,  $b$  and  $c$

are the axes of the primitive cell. Then vectorially

$$A = a - b$$

$$B = a + b$$

$$C = c$$

If  $HKL$  are indices of reflections referred to the non-primitive (and centered) cell and  $hkl$  indices referred to the primitive cell, then by the matrix of trans-

<sup>3</sup> *J. Chem. Soc.*, 1817 (1936).

formation of indices (2.7)

$$H = h - k$$

$$K = h + k$$

$$L = l$$

and

$$H + K = 2h \quad (10.1)$$

Now the indices which correspond to the primitive cell must be integers; hence, if the non-primitive cell is chosen,  $H + K$  must always be even and the 'reflections' which would correspond to odd values of  $H + K$  are said to be extinguished; similarly it can be shown that for a face-centered cell  $h + k$ ,  $k + l$  and  $h + l$  are all even numbers for all reflections which can occur. For a body-centered cell  $h + k + l$  is always even.

Extinctions due to non-primitive unit cells affect the general reflections  $hkl$ . More limited classes of reflections are extinguished by the presence of a glide plane or a screw axis. Figure 16 illustrates the effect of an axial glide on the apparent periodicity of a projection perpendicular to the glide plane.

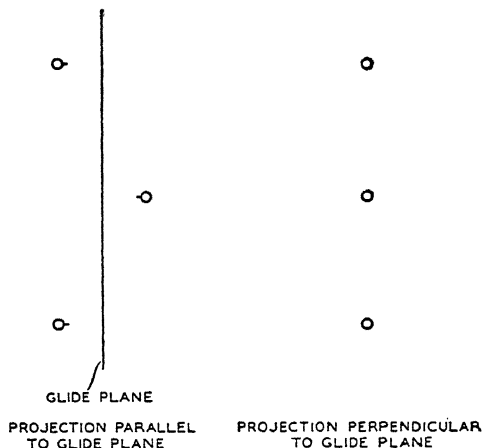


FIG. 16.

It is evident that, viewed in this direction, but in this direction alone, the identity period (in direction  $a$ ) appears to be halved. Thus if the glide plane is  $(010)$  and the translation component is parallel to  $a$ , then for the  $(h0l)$  reflections the  $a$  periodicity will be effectively halved. By transformation of axes it is readily seen that the  $(h0l)$  reflections will only occur where  $h$  is even. No other class of reflections is affected. Extinctions due to a diagonal glide can similarly be deduced.

The effect of a twofold screw axis is shown in Fig. 17. The basal planes perpendicular to the screw axis are now interleaved by an equidistant plane containing the same number of atoms. If the screw axis is parallel to  $b$ , for the  $(0k0)$  reflections the interplanar distance is effectively halved and only even orders occur. A threefold screw axis,  $3_1$  or  $3_2$  causes extinctions of all orders of reflections from the planes perpendicular to the axis which are not divisible by 3, a fourfold screw axis  $4_1$  or  $4_2$  the corresponding reflections not divisible by 4 and a sixfold screw axis,  $6_1$  or  $6_5$ , those not divisible by 6. In all cases the effect of a screw axis is much more limited than that of a glide plane, classes such as  $00l$ ,  $0k0$  or  $h00$  alone showing extinctions.

There are three limitations to the determination of space groups from the X-ray data alone. (1) Only symmetry elements which involve translation components can cause space group extinctions, thus a reflection plane or a

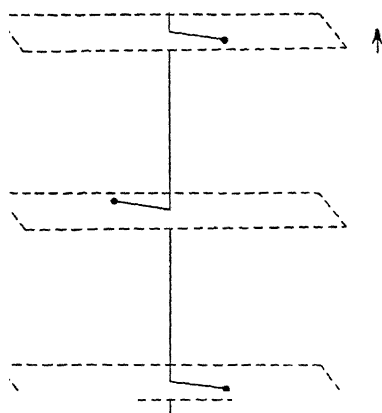


FIG. 17.

simple rotation axis cannot be detected, e.g.,  $P2_1$  cannot be distinguished from  $P2_1/m$ . (2) General extinctions due to non-primitive lattices may obscure more specialized classes of extinctions due to glide planes or screw axes. Thus  $I222$  has  $h + k + l$  always even so  $0k0$ ,  $0k0$  and  $0l0$  have only even orders of  $h$ ,  $k$  and  $l$ , respectively, and the possibility that the space group may be  $I2_12_12_1$  cannot be established. (3) Friedel's law states that  $hkl$  has the same intensity as  $\bar{h}\bar{k}\bar{l}$ , except in the region of an absorption edge. This has the effect of adding a center of symmetry to the diffraction effects and in many cases other physical observations

must be made to determine whether a center of symmetry is actually present in the crystal or not.

#### FOURIER SERIES METHODS

(11) **Three- and Two-dimensional Fourier Series:** In light diffraction the separate interference fringes can be physically recombined by means of a lens to give an image of the object. With X-rays it is impossible to do this, but the equivalent mathematical synthesis can be carried out if there is complete information about the directions, amplitudes and relative phases of the diffracted waves. This was first suggested by W. H. Bragg<sup>1</sup> who realized that as a crystal consists of a periodic distribution of scattering matter it might be possible to evaluate the electron distribution by means of a Fourier series, of the form  $A_0 + A_1 \cos 2\pi(x + \alpha_1) + A_2 \cos 2\pi(2x + \alpha_2) + A_3 \cos 2\pi(3x + \alpha_3) \dots$  etc.

Now

$$F(hkl) = |F(hkl)| e^{i\alpha'(hkl)}$$

where  $F(hkl)$  is complex. In Section 10 we considered the calculation of the structure factor from postulated atomic positions. Scattering matter was assumed to exist only at definite points corresponding to atomic centers, and this is a necessary approximation in testing trial structures, but clearly, in order to make use of the concept of the electron density as a continuous function repeated in every unit cell it is necessary to derive the structure factor by integration. Thus:

$$F(hkl) = \frac{V}{abc} \int_0^a \int_0^b \int_0^c \rho(xyz) e^{i\theta(hkl)} dx dy dz \quad (11.1)$$

<sup>1</sup> *Phil. Trans. Roy. Soc.* (1915).

where  $\rho(xyz)$  is the electron density at the point  $x, y, z$  and  $a, b, c$  are the crystal periodicities and

$$\theta(hkl) = 2\pi \left( \frac{hx}{a} + \frac{ky}{b} + \frac{lz}{c} \right)$$

$$\begin{aligned} \text{Let}^2 \quad \rho(xyz) &= \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} |A(pqr)| \cos \left[ 2\pi \left( \frac{px}{a} + \frac{qy}{b} + \frac{rz}{c} \right) - \alpha(pqr) \right] \\ &= \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} A(pqr) e^{-2\pi i \left( \frac{px}{a} + \frac{qy}{b} + \frac{rz}{c} \right)} \end{aligned}$$

where

$$A(pqr) = |A(pqr)| e^{-i\alpha(pqr)}$$

By substitution in Equation (11.1)

$$F(hkl) = \frac{V}{abc} \int_0^a \int_0^b \int_0^c \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} A(pqr) e^{-2\pi i \left( \frac{px}{a} + \frac{qy}{b} + \frac{rz}{c} \right)} \times e^{2\pi i \left( \frac{hx}{a} + \frac{ky}{b} + \frac{lz}{c} \right)} dx dy dz$$

On integration all terms vanish except where  $p = h, q = k, r = l$  and  $p = -h, q = -k, r = -l$ . By Friedel's law  $|F(hkl)| = |F(\bar{h}\bar{k}\bar{l})|$

hence

$$|A(hkl)| = |F(hkl)| \frac{1}{V}$$

Thus

$$\rho(xyz) = \frac{1}{V} \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} F(hkl) e^{-2\pi i \left( \frac{hx}{a} + \frac{ky}{b} + \frac{lz}{c} \right)} \quad (11.2)$$

where  $F(hkl)$  is complex or

$$\rho(xyz) = \frac{1}{V} \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} |F(hkl)| \cos \left[ 2\pi \left( \frac{hx}{a} + \frac{ky}{b} + \frac{lz}{c} \right) - \alpha(hkl) \right] \quad (11.3)$$

Since  $F(hkl)$  and  $F(\bar{h}\bar{k}\bar{l})$  are conjugate

$$F(hkl) = A + iB$$

$$F(\bar{h}\bar{k}\bar{l}) = A - iB$$

Lonsdale<sup>3</sup> has used these relations to calculate simplified functions of  $A$  and  $B$  for all space groups.

Thus from Equation (11.3)

$$\begin{aligned} \rho(xyz) &= \frac{1}{2V} \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} [(A + iB)e^{-i\theta} + (A - iB)e^{i\theta}] \\ &= \frac{1}{V} \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} (A \cos \theta + B \sin \theta) \end{aligned} \quad (11.4)$$

<sup>2</sup> *Proc. Roy. Soc.*, **A123**, 537 (1929).

<sup>3</sup> *Simplified Structure Factor Tables* (London: George Bell & Sons, Ltd., 1936).

and the electron density is everywhere real.

$$\rho(-x - y - z) = \frac{1}{V} \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} (A \cos \theta - B \sin \theta)$$

If the structure contains a center of symmetry

$$\rho(xyz) = \rho(-x - y - z) \text{ and } B = 0.$$

Also

$$A = |F(hkl)| \cos \alpha(hkl)$$

$$B = |F(hkl)| \sin \alpha(hkl)$$

and therefore

$$\alpha(hkl) = \tan^{-1} \frac{B}{A} \quad (11.5)$$

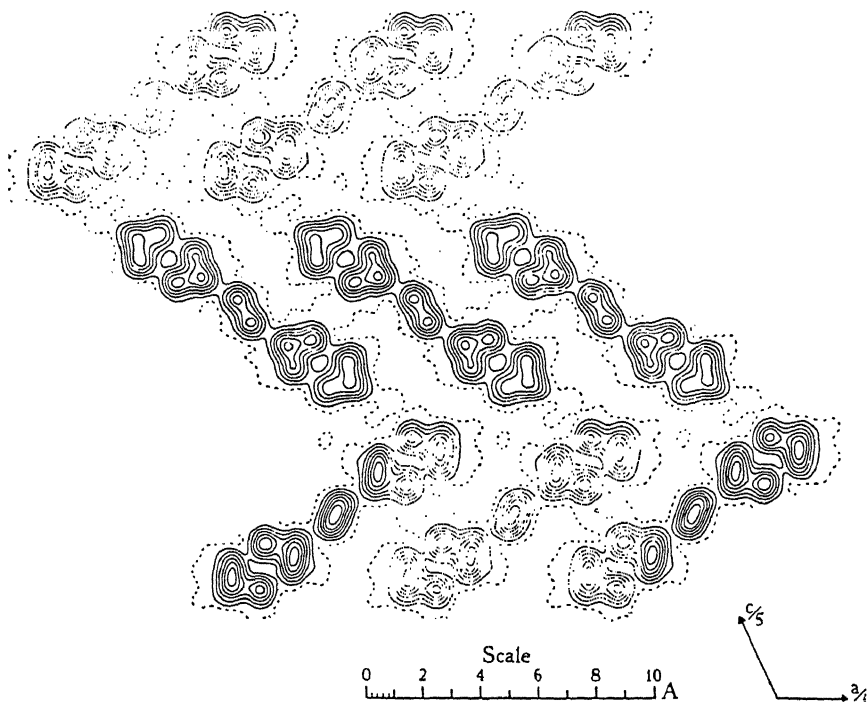


FIG. 18. A group of stilbene molecules in the  $b$  axis projection. Each line approximately 1 electron per  $\text{\AA}^2$  (Robertson).

If the structure is centro-symmetrical then

$$\alpha(hkl) = \tan^{-1} 0 = 0^\circ \text{ or } 180^\circ$$

and

$$F(hkl) = +|F(hkl)| \text{ or } -|F(hkl)|$$

The three-dimensional series (11.2) is very tedious to compute and a simplification to two-dimensional series has been very frequently used,<sup>2</sup>

$$\text{e.g., } \rho(yz) = \frac{1}{A} \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} |F(0kl)| \cos \left[ 2\pi \left( \frac{ky}{b} + \frac{lz}{c} \right) - \alpha(0kl) \right] \quad (11.6)$$

where  $A$  is the area of the projection of the unit cell perpendicular to  $a$ . Equation (11.6) represents the electron density on a crystal plane obtained by projecting the whole cell density on that plane. Two such projections can give all atomic coordinates in a given structure provided no overlapping of atoms occurs. Figure 18 shows one of the earliest of such projection maps, the (010) projection of the stilbene structure by Robertson.<sup>4</sup>

The fundamental difficulty in Fourier synthesis is that the relative phases of the diffracted waves are unknown and cannot be determined directly as this information is necessarily lost in making the diffraction experiment. Methods of finding an approximate structure are described in Sections 20 to 26, and once such an approximate structure is known the Fourier series method can be used as one of successive refinement. The series are computed using observed values for the amplitudes and the phase constants calculated from the postulated structure. The resulting electron density distribution gives slightly different atomic parameters which lead to more accurate phase constants and the process can be repeated until there are no changes in phase constants for all observed reflections.

(12) **Section-projections and Projected Sections:** Booth<sup>1</sup> has developed two modifications of the standard Fourier methods which utilize the complete three-dimensional crystal data available but greatly reduce the time required for a three-dimensional synthesis. The first method is that of section projections and is valuable in cases where certain atoms are obscured by overlapping effects in projections of the whole unit cell. The general expression for an electron density projection on the  $c$  crystal face between the planes  $z = z_1$  and  $z = z_2$  is

$$\begin{aligned} \int_{z_1}^{z_2} \rho(xyz) dz &= \frac{1}{V} \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} \frac{c}{2\pi l} |F(hkl)| \\ &\times \left\{ \sin \left[ 2\pi \left( \frac{hx}{a} + \frac{ky}{b} + \frac{lz_2}{c} \right) - \alpha(hkl) \right] \right. \\ &\quad \left. - \sin \left[ 2\pi \left( \frac{hx}{a} + \frac{ky}{b} + \frac{lz_1}{c} \right) - \alpha(hkl) \right] \right\} \quad (12.1) \end{aligned}$$

Thus in favorable cases a molecule or atom which overlaps can be "screened off" by the correct choice of levels between which Equation (12.1) is evaluated, and the computational work involved is considerably less than in the case of a full

<sup>4</sup> *Proc. Roy. Soc.*, **A140**, 79 (1933).

<sup>1</sup> *Trans. Faraday Soc.*, **41**, 434 (1945).



three-dimensional synthesis. This has been done by Jeffrey in the case of dibenzyl<sup>2</sup> (Fig. 19).

The method of projected sections can sometimes be used to obtain several atoms in the same section of a three-dimensional synthesis instead of computing separate sections for each atom. For a Fourier section at height  $z_1$

$$p(xy z_1) = \frac{1}{V} \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} |F(hkl)| \cos \left\{ 2\pi \left( \frac{hx}{a} + \frac{ky}{b} + \frac{lz_1}{c} \right) - \alpha(hkl) \right\} \quad (12.2)$$

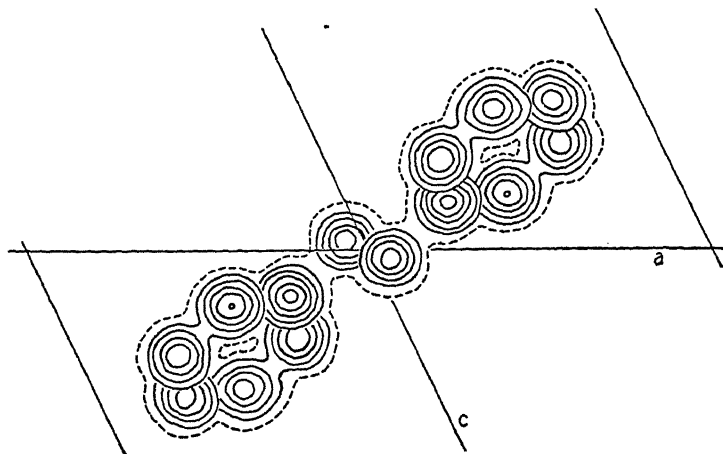


FIG. 19.

Sections through atoms at  $z_1, z_2$ , etc., can be combined, provided the  $x$  and  $y$  coordinates are sufficiently different, to give

$$R(xy z_1 \cdots z_n) = \frac{1}{V} \sum_{\tau=1}^n \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} |F(hkl)| \times \cos \left[ 2\pi \left( \frac{hx}{a} + \frac{ky}{b} + \frac{lz_{\tau}}{c} \right) - \alpha(hkl) \right] \quad (12.3)$$

(13) **The Patterson-Harker Method:** Patterson<sup>1</sup> introduced a powerful aid to crystal analysis by making use of the fact that  $F^2(hkl)$  is a measure of the reflecting power of the plane  $hkl$  after correction by the Lorentz and polarization factors. Consider a one-dimensional distribution of electron density extending over the period from 0 to  $a$ . If two points have parameters  $x$  and  $x + u$ , respectively, then a function of the form

$$p(x)p(x+u)dx$$

where  $p(x)$  is the electron density at the point  $x$  and  $p(x+u)$  the electron

<sup>2</sup> G. A. Jeffrey, *Proc. Roy. Soc.*, **A188**, 222 (1946).

<sup>1</sup> Z. *Krist.*, **90**, 517 (1935).

density at the point  $x + u$ , represents a weighted distribution of electron density about  $x$ . An average over the whole period is given by

$$A(u) = \frac{1}{a} \int_0^a p(x)p(x+u)dx \quad (13.1)$$

and since

$$p(x) = \sum_{-\infty}^{+\infty} F(h)e^{-2\pi i(hx/a)}$$

$$A(u) = \sum_{-\infty}^{+\infty} |F(h)|^2 \cos 2\pi \frac{hu}{a} \quad (13.2)$$

Clearly  $A(u)$  can only be large where both  $p(x)$  and  $p(x+u)$  are large, i.e., a peak in the Patterson function (13.2) at the point  $u$  represents two peaks a distance  $u$  apart in the corresponding electron density function. This treatment can be extended to three dimensions giving

$$A(uvw) = \frac{1}{V} \int^a \int^b \int^c p(xyz)p(x+u, y+v, z+w) dx dy dz$$

$$\sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} |F(hkl)|^2 \cos 2\pi \left( \frac{hu}{a} + \frac{kv}{b} + \frac{lw}{c} \right) \quad (13.3)$$

The series (13.3) can be calculated directly from the experimental data and the resultant distribution is a vectorial representation of all interatomic distances in the crystal.

In all but very simple structures a two dimensional Patterson synthesis leads to overlapping of peaks and for the three dimensional computation great labor is involved. Harker<sup>2</sup> has extended the method to avoid these difficulties by making use of the symmetry elements which occur in most crystals. For example, if the  $b$  axes of the crystal is a twofold symmetry axis then an atom at  $(x, y, z)$  has a crystallographically equivalent atom at  $(\bar{x}, y, \bar{z})$ , the Patterson function will have a maximum at  $(2x, 0, 2z)$  and the plane  $y = 0$  will contain a peak for every independent atom in the structure. Hence

$$A(x0z) = \sum_{h=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} |F(hkl)|^2 \cos 2\pi \left( \frac{hx}{a} + \frac{lz}{c} \right)$$

$$= \sum_{h=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} \cos 2\pi \left( \frac{hx}{a} + \frac{lz}{c} \right) \times \left[ \sum_{k=-\infty}^{\infty} |F(hkl)|^2 \right] \quad (13.4)$$

Equation (13.4) leads to the  $x$ - and  $z$ -coordinates of all atoms and the series is much more easily summed than the three dimensional Patterson series. Similarly the presence of a twofold screw axis leads to the use of the series

$$A(x\frac{1}{2}z) = \sum_{h=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} \cos 2\pi \left( \frac{hx}{a} + \frac{lz}{c} \right) \times \sum_{k=-\infty}^{\infty} (-1)^k |F(hkl)|^2 \quad (13.5)$$

<sup>2</sup> J. Chem. Phys., 4, 381 (1936).

and Harker has shown that such simplified expressions can be derived for every crystal outside the triclinic system. Examples of the use of the Patterson-Harker method are discussed in Section 21 where the problem of analysis of unknown structures is considered in detail.

#### EXPERIMENTAL METHODS OF X-RAY ANALYSIS

(14) **The Laue Method:** The Bragg law can be satisfied in two ways. If monochromatic radiation is used the only variable is the angle of incidence of the X-ray beam and for a given plane to reflect the crystal must be turned to a

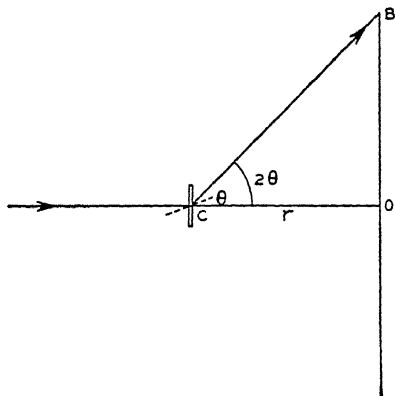


FIG. 20.

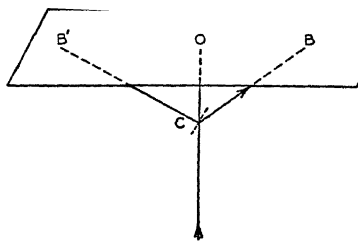


FIG. 21.

position such that  $\theta$ , the complement of the angle of incidence, is equal to  $\sin^{-1} \frac{n\lambda}{2d}$ . On the other hand a large number of reflections can occur simultaneously if white X-rays are used as a set of planes of spacing  $d$  will selectively reflect the radiation of wavelength  $\lambda = \frac{2d \sin \theta}{n}$  if this wavelength is within the

continuous range. This is the basis of the Laue method as shown diagrammatically in Fig. 20. A stationary crystal, usually a thin section, is placed in the path of the beam, preferably with a crystal axis parallel to the beam. The X-ray source is generally a tungsten target operated at a voltage selected to reduce the characteristic spectrum as much as possible compared with the continuous spectrum. The reflections are recorded on a flat plate at right angles to the path of the incident X-ray beam and at a distance  $r$  from the crystal. If the direct beam meets the plate in  $O$  and a reflection occurs at  $B$  then  $OB = r \tan 2\theta$  where  $\theta$  is the Bragg angle.

The indexing of the reflections in a Laue photograph<sup>1</sup> is most easily carried out by graphical methods using gnomonic projections. In Fig. 21 the photo-

<sup>1</sup> Wyckoff, *The Structure of Crystals* (New York: Reinhold Publishing Corp., 1931), p. 124.

graphic plate is assumed to be the plane of the gnomonic projection. Again the direct X-ray beam intersects this plane in  $B$ .  $B'$  is the gnomonic projection of the reflecting plane, i.e., the point where the normal to this plane intersects the projection plane and hence  $OB' = r \cot \theta$  and  $B$ ,  $O$  and  $B'$  are collinear. Since  $OB = r \tan 2\theta$

$$OB = OB' \frac{\tan 2\theta}{\cot \theta} \quad (14.1)$$

It is now easy to construct the gnomonic projection from the Laue photograph. A scale can be made the center of which is placed at the center of the film and on the other side the gradations are constructed from the relation (14.1) to give the position of the corresponding gnomonic projection points. If sufficient is known about the crystal initially to construct its gnomonic projection on the plane corresponding to the photographic plate then the indices of all reflections can be assigned directly by superimposing the film and the projection and using the scale described above. The wavelength which has been reflected by each plane can then be calculated.

While the Laue method has been used to work out several crystal structures the experimental difficulties in intensity estimations are considerable as it is necessary to know the proportions of different X-ray wavelengths in the primary beam and to make allowance for the differential absorption of the non-homogeneous primary beam by the crystal. In modern work the Laue technique is used mainly for symmetry information and for structural work has long been superseded by the various methods which make use of monochromatic radiation.

(15) **The Bragg Method:**<sup>1</sup> The method originally used for verification of Bragg's law remains one of the most powerful available for really accurate observations on individual X-ray reflections. A monochromatic beam of X-rays is passed through successive collimating slits (Fig. 22) and is then reflected from the face of a crystal situated on a rotating table, the angular setting of which can be read by a scale and vernier. The reflected beam passes into the ionization chamber which moves at twice the angular velocity of the crystal in order to maintain the geometrical conditions for Bragg's law. The ionization chamber contains a gas such as methyl bromide which is readily ionized by the radiation, and the ionization current, recorded by an electrometer, is a measure of the intensity of the reflected beam. As a reflection occurs

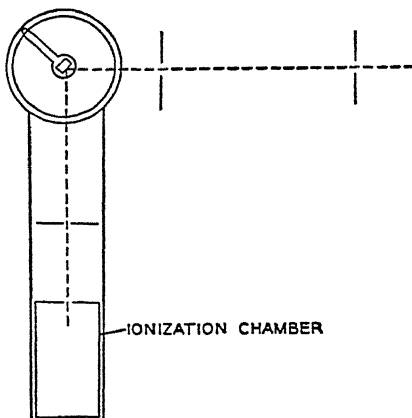


FIG. 22.

<sup>1</sup> W. H. Bragg and W. L. Bragg, *Proc. Roy. Soc.*, A88, 428 (1913).

over a small angular range it is necessary to plot the recorded intensity against the angular setting of the crystal and calculate the integrated intensity.

As initially used, the area of the reflecting crystal face was large compared with the cross-section of the beam. Thus the intensities of successive orders of reflections from a given crystal face could be examined with considerable accuracy but in some crystals faces had to be cut or ground.

(16) **The Rotation-oscillation Method:** The individual measurement of reflections by the ionization spectrometer is tedious and the techniques most commonly used at present are based on photographic recording of the reflections of monochromatic radiation from a rotating crystal. In the simple rotation

method the axis of rotation is usually normal to the incident beam and an extremely small crystal is completely bathed in the X-radiation. The reflections can be recorded on a flat photographic plate or, more efficiently, on a cylindrical film concentric with the rotation axis.

In Fig. 14 the conditions for generation of an X-ray reflection have been illustrated. Figure 23 is a view of the reciprocal lattice perpendicular to the rotation axis. As the crystal rotates the reciprocal lattice can be imagined to

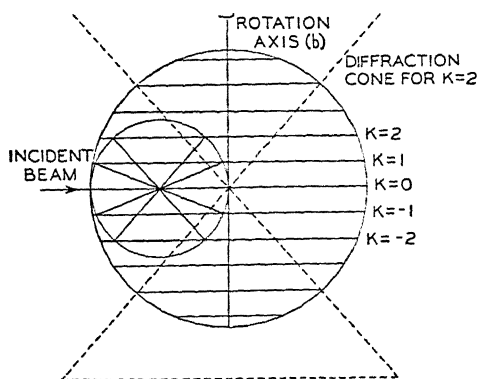


FIG. 23.

rotate about the same axis and a reflection occurs when a reciprocal lattice point cuts the sphere of reflection. If the crystal rotation axis is  $b$  then the reciprocal lattice consists of layers each of which is perpendicular to  $b$  and the points in each such layer have a common index  $k$ .

The intersections of the points in each layer with the sphere of reflection lie on a circle whose plane is perpendicular to the rotation axis. Now as the direction of reflection, in real space, is parallel to the line joining the center of the sphere of reflection to the point of intersection of the sphere with the reciprocal lattice point concerned, it is clear that all reflections formed in a crystal rotation will lie on the surfaces of a series of concentric cones whose semi-vertical angle decreases as the index  $k$  increases. These cones intersect a flat plate in a series of hyperbolas (Fig. 24) or a cylindrical film in straight lines, the characteristic layer lines of rotation photographs. From the distances between the layer lines it is easy to calculate the periodicity along the rotation axis. From Fig. 25,

$$n\lambda = b \sin \varphi \quad (16.1)$$

where  $\varphi$  is the complement of the semi-vertical angle of the cone of reflection,  $n$  the order of the layer line and  $b$  the periodicity along the rotation axis.  $\varphi$  is

readily calculated from the vertical distance of the layer line from the center of the film and the known radius of the camera (where a cylindrical film is used).

By rotation of the crystal about one axis with the incident beam perpendicular to that axis, it is clear that all reflections which can occur lie within the torus of reflection shaded in Fig. 26, and other reciprocal lattice points within the limiting sphere can only give rise to reflections if a different rotation axis is used. This is important in cases where it is desired to record all possible reflections for a given wavelength for calculation of a three-dimensional Fourier series.

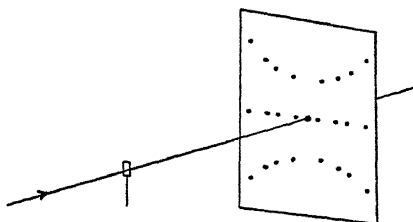


FIG. 24.

Following Buerger<sup>1</sup> we may define a reciprocal lattice point by means of its cylindrical coordinates with respect to the rotation axis,  $\sigma$ , the distance of the point from the origin, can be resolved into two components  $\zeta$ , parallel to the axis and  $\xi$  perpendicular to the axis of rotation. The angle  $\varphi$  which the plane containing the vectors  $\zeta$  and  $\xi$  makes with the plane parallel to the axis containing the incident X-ray beam is the third cylindrical coordinate.  $\zeta$  and  $\xi$  can be calculated from the vertical and horizontal coordinates of each spot on

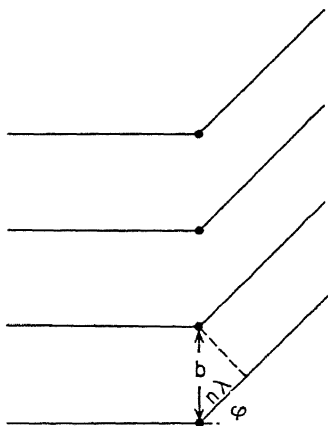


FIG. 25.

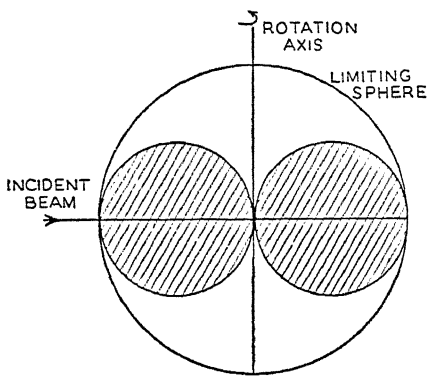


FIG. 26.

the photograph. It is most convenient to construct a chart of  $\zeta$  and  $\xi$  values for a known camera radius<sup>2</sup> and these parameters can then be read off directly by superposition on the film. The parameter  $\varphi$ , which represents the angular rotation of the crystal from an initial position before reflection occurs, is not determined in the simple rotation method with the result that in complex struc-

<sup>1</sup> M. J. Buerger, *X-ray Crystallography* (New York: John Wiley & Sons, Inc., 1942).

<sup>2</sup> J. D. Bernal, *Proc. Roy. Soc.*, A113, 123 (1926).

tures it is not possible to index the reflections unequivocally as two or more reciprocal lattice points may have the same  $\zeta$  and  $\xi$  values.

Two modifications of the rotation method have been used in order to aid indexing. The tilted crystal method described by Bunn<sup>3</sup> and coworkers consists of tilting the axis of rotation by a known small angle in a known direction. The layer lines are now slightly distorted and it is possible to resolve reflections previously superimposed, but the calculations required for indexing are tedious. A commoner procedure is to restrict rotation to an oscillation of  $10^\circ$  or  $15^\circ$  when the number of spots on the film is greatly reduced. If the initial positions of the crystal axes with respect to the incident beam are known it is easy to find which reflections can occur as shown in Fig. 27.

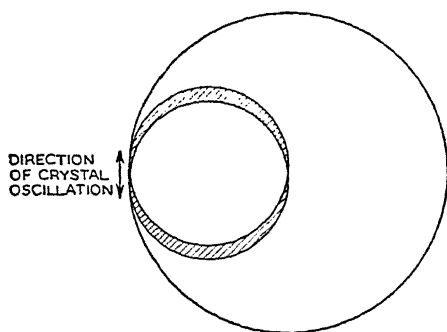


FIG. 27.

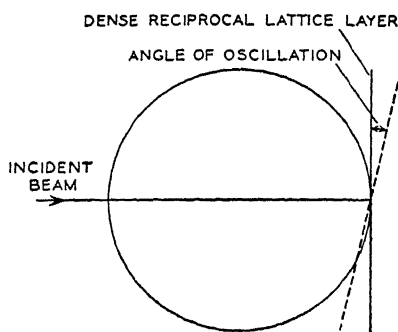


FIG. 28.

If the reciprocal lattice is imagined to be stationary and the sphere of reflection to oscillate through the required angle, only reciprocal lattice points within the shaded areas will reflect, reflections due to points in one crescent appearing on the left-hand side of the film and those due to points in the other on the right-hand side. Thus the chance of ambiguity in indexing is small but a large number of overlapping photographs is required to record the data completely.

A very powerful use of the oscillation technique can be made where the crystal unit cell is very large, e.g., in crystalline protein work. The crystal is oriented so that at the beginning of the oscillation the densest reciprocal lattice layers are perpendicular to the X-ray beam (Fig. 28). The zero layer of the reciprocal lattice is originally tangential to the sphere of reflection and at the end of the oscillation it cuts the sphere in a small circle. Since all the reflections within this circular area occur at very low angles the projection of the intersections of the reciprocal lattice points with the sphere of reflection on the film will be very little distorted and a small circular area near the center of the film will contain, in effect, an approximate picture of this reciprocal lattice layer which can be indexed by inspection.

<sup>3</sup> C. W. Bunn, H. S. Peiser and A. Turner-Jones, *J. Sci. Instruments*, **21**, 10 (1944).

Oscillation photographs also give useful information about symmetry. If the rotation axis is a symmetry axis, i.e., if there is a symmetry plane normal to the axis then the spots on the upper and lower halves of the oscillation photograph will be identical both in position and intensity. An  $n$  fold axis of symmetry parallel to the rotation axis can be detected by two oscillation photographs separated by an angle  $360^\circ/n$ . If the symmetry axis is present the two photographs should be identical.

(17) The Weissenberg Method:<sup>1</sup>

To define a reciprocal lattice point three parameters are required. In the simple rotation method we can measure only two coordinates on a film for each reflection and it is only possible to prove that a given reflection corresponds to a certain reciprocal lattice point if it can be shown that no other reciprocal lattice point which

gave rise to a reflection during the experiment has the same two measurable

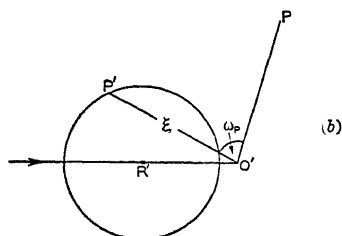
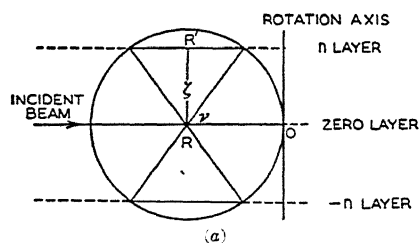


FIG. 30.

reach the film. The  $x$  and  $z$  film coordinates give the corresponding angular coordinates  $\omega$  and  $\gamma$  by the relations

$$\frac{x}{2\pi r} = \frac{\gamma}{360^\circ}$$

where  $r$  is the radius of the camera, and

$$\frac{z}{k} = \frac{\omega}{180^\circ}$$

<sup>1</sup> K. Weissenberg, *Z. Physik*, 23, 229 (1924).

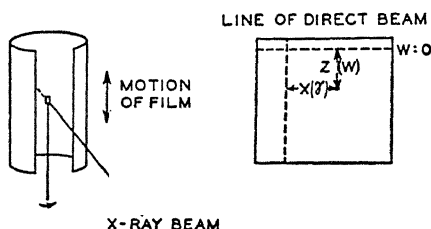


FIG. 29.

coordinates. A far more satisfactory method is to select one layer line of a rotation photograph and move the film in some way which spreads the reflections in the layer line over two dimensions.  $z$  is known for the selected layer line by measurement of the preliminary rotation photograph and there are now two film coordinates which fix the remaining two parameters. This is achieved in the normal beam Weissenberg method shown in Fig. 29. This is a development of the simple rotation method in which the cylindrical film moves along the axis of rotation in synchronization with the rotation of the crystal. Screens are placed between the film and the crystal so that only one layer line can



where  $k$  is the distance travelled by the film during a crystal rotation of  $180^\circ$ . It is now possible to construct the reciprocal lattice layer from the Weissenberg photograph by Schneider's construction<sup>2</sup> as shown in Fig. 30. In (a) the reciprocal lattice is viewed in a direction perpendicular to the rotation axis and the radius of the intersection of the sphere of reflection with the reciprocal lattice layer is calculated from the known value of  $\xi$  for the  $n$ th layer. This diagram is projected down the rotation axis in (b). The point on the sphere of reflection cut by  $P$  is found from the measured value of  $\gamma_p$  and if  $O'P'$  is rotated back through the angle  $\omega_p$  we arrive at the initial position of the reciprocal lattice point  $P$ . Similarly the whole reciprocal lattice layer can be constructed.

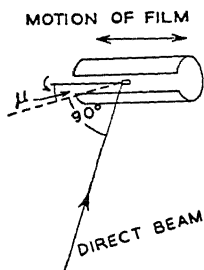


FIG. 31.

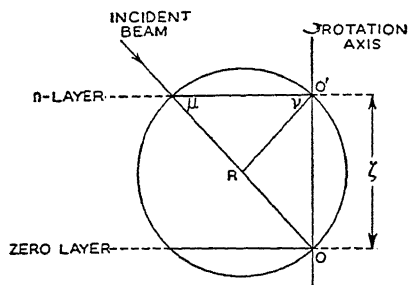


FIG. 32.

A technique which has considerable advantages over the normal beam Weissenberg method is the equi-inclination Weissenberg method, illustrated in Fig. 31. The camera moves in the same direction as before, parallel to the axis of rotation, but the whole instrument is mounted on a movable base so that the rotation axis makes an angle  $90^\circ + \mu$  with the incident beam and  $\mu$  is chosen so that the incident and diffracted X-ray beams are equally inclined to the reciprocal lattice layers as shown in Fig. 32 where the rotation is the same as in Fig. 30. In this case,  $O'$ , the center of the reciprocal lattice layer, lies on the sphere of reflection.  $OP'$  is part of a central lattice line, i.e., a reciprocal lattice line which passes through the rotation axis. Now if  $OX'$ , perpendicular to  $OS'$  be the initial position of the line  $OP'$  then  $\gamma = 2\omega$  and this result is independent of which layer is considered. Thus central lattice lines have the same slope regardless of the reciprocal lattice layer and this greatly simplifies the interpretation of photographs. In certain cases it is possible to index reflections on an  $n$ -layer equi-inclination Weissenberg photograph merely by superposition of the easily indexed zero-layer photograph. Further details of the interpretation of equi-inclination photographs are given by Buerger.<sup>3</sup>

One further advantage of the equi-inclination method over the normal beam method becomes clear on examination of Fig. 33 which corresponds to Fig. 16 for the normal beam Weissenberg and simple rotation methods. The shaded

<sup>2</sup> W. Schneider, *Z. Krist.*, **69**, 41 (1928).

<sup>3</sup> M. J. Buerger, *loc. cit.*

area includes those reciprocal lattice points which reflect during a crystal rotation and it is clear that with the equi-inclination method it is possible to record reflections for all points on an  $n$ -layer which lie within the limiting sphere of the reciprocal lattice.

(18) **The Debye-Scherrer-Hull Method:**<sup>1, 2</sup> If a powdered material is used instead of a single crystal for X-ray diffraction the specimen consists of a large number of extremely small crystals which are randomly oriented. For every possible X-ray reflection, with monochromatic radiation, there will be some crystallites oriented in such a way that the reflection will develop. The angle between the direct beam and the diffracted beam is twice the Bragg angle for this reflection hence all rays diffracted at this angle will lie on the surface of a cone of semi-vertical angle  $2\theta$  which is concentric with the path of the main beam (Fig. 34). The diffraction cones intersect a flat photographic plate perpendicular to the primary beam, in a series of concentric circles, or a cylindrical strip of film in a series of arcs.

The utility of the powder method in structure analysis is greatly limited owing to the difficulty of indexing reflections. As described in previous sections three parameters are required in order to assign indices unequivocally to a given reflection and in the powder method we can only make one measurement, the distance of a diffraction arc from the center of the film. If this distance is  $x$  the Bragg angle can be found from the relation  $x/2\pi r =$

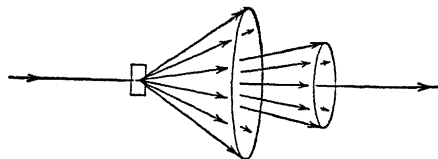


FIG. 34.

$2\theta/360^\circ$  where  $r$  is the radius of the cylindrical camera. If the symmetry of the crystalline material is high (cubic, tetragonal or hexagonal) it may be possible to assign the dimensions of the unit cell with some certainty, but in cases of lower symmetry the problem becomes extremely difficult.

Another disadvantage of the powder method is the very small proportion of the incident energy used in the formation of each reflection, although in the rotation method a given plane only reflects for a very small fraction of the rotation while in the powder method all reflections are developed continuously. However the powder circle or arc on the photograph is spread out over a very much larger area than the single crystal reflection and in general powder photographs require long exposures. Careful collimation is required to reduce the

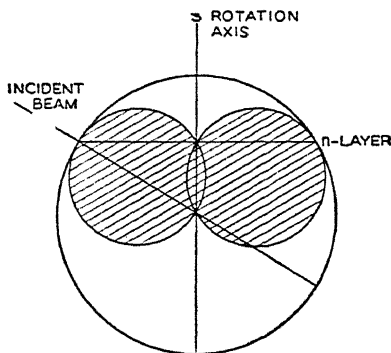


FIG. 33.

<sup>1</sup> P. Debye and P. Scherrer, *Z. Physik*, 17, 277 (1916).

<sup>2</sup> A. W. Hull, *Phys. Rev.*, 10, 661 (1917).

background and in addition many powder cameras are evacuated or filled with hydrogen to minimize scattering and absorption by the air.

The main uses of the powder method are in identification of unknown materials and in precision measurements of cell-dimensions previously known

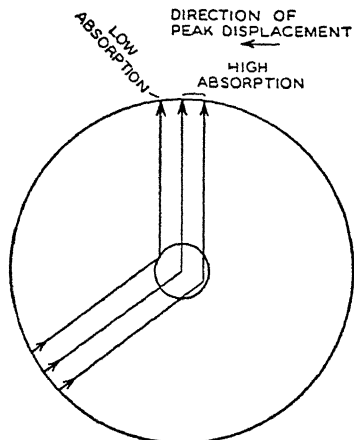


FIG. 35.

approximately from some other type of photograph. In analysis, an X-ray photograph is probably the best method of deciding whether an unknown substance is actually identical with a substance whose powder pattern is known or can be determined. Direct comparison of the two photographs or of the two lists of spacings and approximate intensities is sufficient. Extremely accurate cell parameters can be obtained by using high angle powder reflections where these can be indexed unequivocally. The principal error is due to absorption of the beam by the specimen which causes a displacement of the diffraction peak as shown in Fig. 35. This effect can be allowed for by calculation or by mixing the specimen with a standard the para-

meters of which are very accurately known. The diffraction lines of the standard will shift in the same manner as the specimen.

#### INTERPRETATION OF THE X-RAY DATA

(19) **General Procedure:** The exact procedure for determination of an unknown crystal structure varies both with the complexity of the problem and the accuracy of the information required. However, the following stages are customary in most detailed analyses:

- (1) measurement of the unit cell dimensions;
- (2) determination of the space-group;
- (3) measurement of the density of the crystal, which, with the chemical composition and cell dimensions, gives the number of atoms or molecules associated with each unit cell;
- (4) deduction of the asymmetric unit of pattern, i.e., the group of crystallographically independent atoms, which is usually a fraction of the total number of atoms in the unit cell;
- (5) determination of approximate atomic parameters which are in agreement with the observed intensities of X-ray reflections;
- (6) refinement of the approximate atomic parameters by Fourier series or other methods.

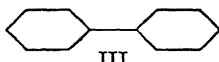
Stages (1) and (2) have already been discussed and it has been pointed out that the space-group cannot always be uniquely determined by X-ray data

alone. In cases where more than one space-group is possible it is necessary to make a morphological study of the crystal faces, with the use of etch figures and sometimes pyro- and piezo-electric effects in order to determine the crystal class. Where such measurements are inconclusive it is customary to choose the space-group of lowest symmetry from among the several possibilities deduced from the X-ray diffraction data.

Frequently an important structural question can be decided from a knowledge of the space-group and the number of molecules per unit cell. The structure of diphenylene (I) for example, was shown to be incompatible with the



formula II,<sup>1</sup> as the crystal space-group  $P2_1/a$  with only two molecules in the unit cell requires that each molecule has a center of symmetry. Similarly diphenyl<sup>2</sup> (III) is almost certainly flat, in the crystal, assuming that each of the benzene rings is flat, for any rotation of one ring relative to the other about the central bond would destroy the inherent molecular center of symmetry required by the space-group.



It should be noted that the space-group requirements can give information concerning only the minimum symmetry of a molecule. The fact that the crystal symmetry does not require any molecular symmetry does not mean that in the isolated molecule any particular symmetry element is absent, and, in fact, it is well known that the full symmetry of an organic molecule is rarely reflected in the crystal symmetry. For example, hexamethyl benzene appears to be hexagonal, but crystallizes in the triclinic system.<sup>3</sup> The pyrene molecule contains a center of symmetry, within the limits of accuracy of the X-ray measurements<sup>4</sup> but this molecular center of symmetry is not used in building up the crystal structure and occurs in a general crystal position, some distance from the crystallographic center of symmetry which lies between two molecules. In all such cases the packing of molecules in such a way as to minimize the potential energy of the crystal must lead to the less symmetrical arrangement.

In many crystals, particularly with ionic structures, one or more atoms may be in special positions which are automatically determined from symmetry considerations. Thus if there is only one atom of a certain element in a structure of which the asymmetric unit is one quarter of the unit cell, then the quarter atom must be placed in such a position that the symmetry operations of the

<sup>1</sup> J. Waser and C. S. Lu, *J. Am. Chem. Soc.*, **66**, 2035 (1944).

<sup>2</sup> G. L. Clark and L. W. Pickett, *J. Am. Chem. Soc.*, **53**, 167 (1931).

<sup>3</sup> K. Lonsdale, *Proc. Roy. Soc.*, **A123**, 494 (1929).

<sup>4</sup> J. M. Robertson and J. G. White, *J. Chem. Soc.*, 358 (1947).

space-group give rise to one complete atom, or in other words, that atom must be in such a position that it is not reproduced anywhere else in the unit cell by symmetry. There is the reservation here that for such reasoning to be valid there must be no "randomness" in the structure, i.e., all unit cells in the crystal must be identical. Where most of the atoms lie in special positions structure determination may reduce to defining only two or three unknown parameters, and elaborate refinement is probably unnecessary.

Structure analyses of complex organic crystals, however, may involve the determination of about 100 parameters and once an approximate structure is known refinement is usually carried out by Fourier analysis, the essential validity of a structure being established by quantitative agreement between the observed and calculated values of the structure factors. In such work the problem is one of finding a sufficient number of the unknown phase constants in order to carry out a Fourier synthesis. Once this is achieved, refinement of the parameters becomes almost a matter of routine. On a purely mathematical basis there are an infinite number of solutions to the electron density equations given in Section 11. However, on chemical grounds, we know that the electron density distribution in a crystal is concentrated around certain points corresponding to atomic centers, and in certain cases the use of this knowledge allows the postulation of an approximate structure which gives agreement with the observed intensities of X-ray reflections, and the phase constants can be calculated. In the following sections the various methods of finding the approximate structure, or of some of the unknown phase constants are discussed.

(20) **Trial Analysis:** All early X-ray analyses were carried out by a process of trial and error and the method is used today in one stage or another of most structure determinations. The X-ray data are examined for any outstanding distributions of intensity, for example reflections which have very high or very low geometrical structure factors. A structure is postulated which will account for such features and is then rigorously tested by calculation of all the structure factors and comparison of the observed with the calculated values. It may become apparent that the initial agreement is fortuitous in which case the structure is abandoned. On the other hand, it may be that the agreement is fairly convincing but that minor adjustments are needed before it is accepted as being correct.

In the initial stage of postulating the trial structure, physical evidence quite apart from that given by X-ray diffraction is valuable and has been extensively used in the past. Refractive index measurements may indicate the direction of a long molecular axis with respect to the crystal axes; anisotropic light absorption can give evidence of the orientation of certain chemical groups; magnetic susceptibility measurements can lead to the deduction of the tilt of a flat molecule to the crystal axes; crystal morphology may also give clues to the internal structure. Always, the whole body of general chemical and crystallographic knowledge is of the highest importance. Effective atomic or ionic radii and coordination numbers, known from previous structure determinations, are of great help in dealing with inorganic crystals, while obviously for organic

structures, the greater the certainty with which the probable molecular configuration and dimensions can be estimated the more rapid will be the analysis. At the other extreme, where the structure of a complex organic molecule is unknown even from the point of view of organic chemistry, the method of trial is most unlikely to reach a successful conclusion, and if possible the problem should be attacked by one of the more suitable methods described in later sections.

As an example of a very simple structure analysis we may consider that of zinc blende (Fig. 36); which has been completely elucidated from a relatively small number of X-ray reflections.<sup>1</sup> The crystal system is cubic and indexing of several orders of reflection from each of the main crystal faces shows a face-centered unit cell which contains four zinc atoms and four sulfur atoms. We can therefore place

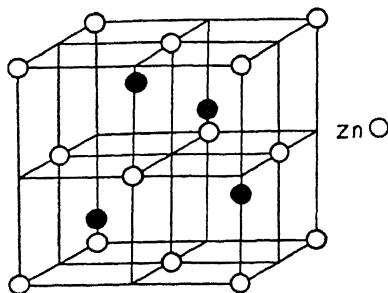


FIG. 36.

one zinc atom at each of the corners of the cell and one at the center of each face give a total of four atoms per cell when allowance is made for the sharing of atoms between neighboring cells. Now we should be equally justified in placing the sulfur atoms instead of the zinc in exactly these positions as the same conditions must be satisfied for the sulfur atoms. There must therefore be two such face centered lattices which interpenetrate each other, one with sulfur atoms at the lattice points and the other with zinc atoms, and the choice of origin determines which is regarded as the basic lattice. The only remaining question to be settled is the spatial relationship between these two lattices. A simpler way of treating the problem is to consider the zinc atoms to be fixed at the positions shown in Fig. 36. Then the position of one sulfur atom relative to the zinc gives the complete structure as the other three sulfur atoms are reproduced by symmetry. In order to find this information it is necessary to examine the intensities of certain reflections as well as systematic absences. Two outstanding features are apparent. The odd orders of reflection from the (100) face are extremely weak, indicating that the sulfur atoms are arranged in layers half way in between the layers of zinc atoms parallel to (100). In this position the waves scattered by the sulfur atoms are of opposite phase to those scattered by the zinc atoms for the odd orders of the reflections which occur from (100) and hence these orders are weakened. Since the crystal is cubic this observation holds for reflections from (001) and (010) also and the only reasonable positions for the sulfur atoms are those given in Fig. 36. The sulfurs are arranged at the centers of the small cubes (each cube is one eighth of the unit cell) and is tetrahedrally coordinated to four zinc atoms. The arrangement of the sulfur atoms around the zinc atoms is similar. If we examine the lattice planes parallel to (111) it can be seen that the layers of sulfur atoms lie one quarter way between the zinc layers and this will have

<sup>1</sup> W. L. Bragg, *Proc. Roy. Soc.*, A89, 468 (1914).

the effect of greatly reducing the second order of reflection from (111). This is in complete agreement with the observed measurements.

In more complex structures, and in particular in most organic structures, the number of atoms involved in the asymmetric crystal unit is so large that it is not always possible to vary all their positions systematically in order to obtain agreement with the observed data. The customary procedure in dealing with molecular structures is to assume the most probable model for the molecule on chemical grounds and to vary its orientation with respect to the crystal axes and its position with respect to a crystal origin. If the asymmetric unit is one molecule six parameters are required to specify the structure while if the asymmetric unit is a fraction of the molecule this number is reduced. If there are within the molecule parameters which cannot be estimated with any accuracy from previous knowledge, each must be varied throughout the possible range in conjunction with the variation of molecular orientation and position and the work required is multiplied many times.

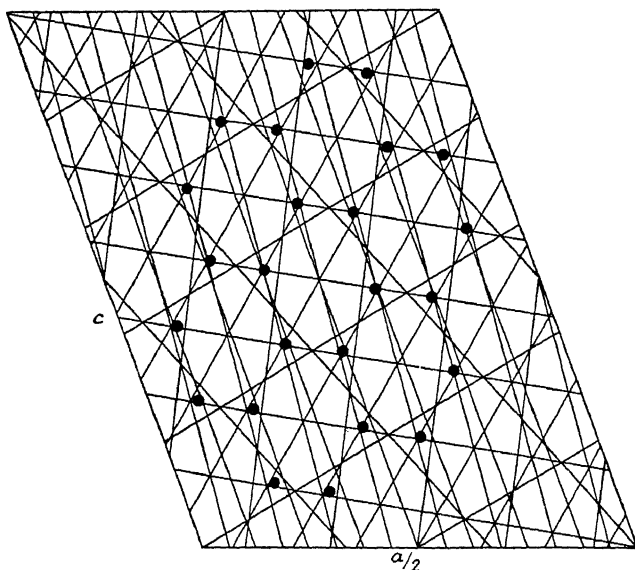


FIG. 37.

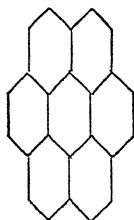
One technique suitable for relatively simple molecular structures has led to the rapid elucidation of many such structures. For a centro-symmetrical crystal the structure factor is given by

$$F = \sum f \cos 2\pi \left( \frac{hx}{a} + \frac{ky}{b} + \frac{lz}{c} \right)$$

the summation being carried out over all atoms in the unit cell. Now for the reflection  $hkl$  this expression is a positive maximum where all the atoms lie on

the  $hkl$  planes and a negative maximum where the atoms are exactly half way in between the  $hkl$  planes. The intensities of reflections from small-spacing sets of planes are very sensitive to the orientation of rows of atoms within the molecule, the spacing of which is of about the same magnitude as that of the reflecting planes. Therefore, it is often possible to find the molecular orientation by drawing in the small spacing planes which give reflections of high geometrical structure factors, on a certain projection of the unit cell, and varying the orientation of a molecular model until nearly all the atoms in projection lie on or half way between each set of planes. This process is illustrated by the (010) projection for coronene<sup>2</sup> ( $C_{24}H_{12}$ ) in Fig. 37. This diagram has been simplified by drawing in the planes themselves where the structure factors of the corresponding reflections are positive and the lines half way in between the planes where the reflections have negative structure factors. It can be seen that all the atoms lie very close to intersections of the traces of these planes.

As an illustration of the value of previous chemical and crystallographic knowledge in shortening a structure analysis we may consider the coronene structure in detail. The space-group is the very common  $P2_1/a$  and there are two molecules in the unit cell. This requires that the asymmetric unit is one half molecule and as the molecular center is fixed at a crystallographic center of symmetry, it is only necessary to find the molecular orientation with respect to the crystal axes. The organic chemical formula (IV) in conjunction with



IV

previous X-ray analyses of condensed ring aromatic hydrocarbons<sup>3, 4</sup> suggests that the molecule is planar and is composed of approximately regular, hexagonal benzene rings of radius about 1.4 Å. The crystals grow in the form of needles elongated along the  $b$  crystal axis which has a periodicity of 4.695 Å. The crystal habit is a common one for large flat molecules (e.g., phthalocyanine<sup>5</sup>) and as the perpendicular interplanar distances in such cases are always close to 3.4 Å, the tilt of the molecular planes to  $b$  is probably  $\cos^{-1}(3.4/4.695)$ , or about  $45^\circ$ . If this assumption is correct there are only two remaining degrees of freedom, viz., the molecular direction which lies in the (010) plane and the angle which this line makes with either the  $a$  or the  $c$  axes. These two param-

<sup>2</sup> J. M. Robertson and J. G. White, *J. Chem. Soc.*, 607 (1945).

<sup>3</sup> J. M. Robertson, *Proc. Roy. Soc.*, A140, 79 (1933).

<sup>4</sup> *Ibid.*, A142, 659 (1933).

<sup>5</sup> J. M. Robertson, *J. Chem. Soc.*, 1195 (1936).



eters are readily found by the method illustrated in Fig. 37 and from the resulting atomic positions sufficient phase constants can be calculated to carry out a Fourier synthesis.

The case of coronene is comparatively simple because the (*h*01) structure factor formula is

$$F = \sum f \cos 2\pi \left( \frac{hx}{a} + \frac{lz}{c} \right) \quad (20.1)$$

summed over the asymmetric unit alone and this is of the same form as when summed over all atoms in the cell; hence, only the asymmetric unit need be considered. In any centro-symmetrical projection, of course, it is possible to use the graphical method of trial described above provided all symmetrically related atoms are moved to the corresponding positions for every movement of the atoms in the asymmetric unit. However, this procedure is complicated and in many cases it is possible to change the form of the simplified structure factor expression into that of Equation (20.1). For example in an (*Ok**l*) zone where

$$F = \sum f \cos 2\pi \frac{ky}{b} \cos 2\pi \frac{lz}{c} \quad (\text{for } k \text{ even})$$

$$F = \sum \left\{ \frac{f}{2} \left[ 2\pi \cos \left( \frac{ky}{b} + \frac{lz}{c} \right) + \cos \left( \frac{ky}{b} - \frac{lz}{c} \right) \right] \right\} \quad (20.2)$$

and this expression requires to be summed over the atoms in the asymmetric unit alone. In a diagram such as Fig. 36, Equation (20.2) means that the structure factor will be a positive maximum for (*Ok**l*) when all atoms in the asymmetric unit are lying on the (*Ok**l*) planes and also on the (*Ok* $\bar{l}$ ) planes. Hence, the same procedure can be carried out as before. Of course the structure factor formula may be too complicated to handle in this way but formulas involving the sum of two cosines, the product of two cosines and the product of two sines are fairly common in projections of molecular structures.

A further complication arises where the molecule has free parameters of translations, i.e., the asymmetric unit is a complete molecule and not part of a molecule as in the case of coronene. Here any indications of pseudo-symmetry are very useful. For instance if there are no systematic absences in the *h*0*l* reflections but all those which have odd values of *h* are greatly reduced in intensity compared with the rest it is clear that there is a scattering group in such a position as to cause the *a* axis to be approximately halved in the (010) projection. This reasoning can be usefully extended to any large spacing sets of planes which need not necessarily be axial, and which give either very weak reflections or none at all. Figure 38 illustrates the *ac* projection of the unit cell of hypothetical structure in which there are two molecules related to each other by a center of symmetry. The reflections (001) and (101) are absent or very weak. Then the center of gravity of each molecule must lie one quarter way in between both of these two sets of planes as indicated by the dotted lines. There are only three reasonable possibilities as marked by the crosses, black

circles and white circles. In practice it is probable that if the molecular orientation had already been deduced by the methods described two out of these three possibilities could be eliminated on packing considerations.

In all cases and, in particular, where the molecule itself contains unknown parameters, any method of rapid evaluation of structure factors obviously increases the power of the trial method.

Bragg and Lipson<sup>6</sup> have prepared charts for all plane groups (space-group projections) showing the division between the positive and negative areas of the cell projection for the contribution of an atom to a given reflection. It is possible by this means to estimate very rapidly and with sufficient accuracy the effect on the structure factor of shifting an atom in any direction. This can be particularly useful

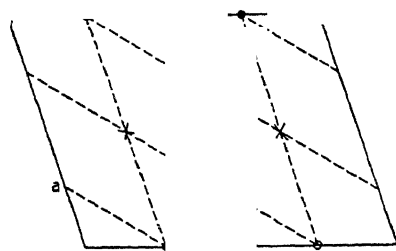


FIG. 38.

where the trial structure appears to be essentially correct but where it is desirable to make further adjustments before starting a Fourier synthesis.

A method suggested by W. L. Bragg<sup>7</sup> is likely to have increasing importance in future work. A model of a unit cell projection is photographed by a multiple pinhole technique so that a large number of cells appear together on a small scale. In the model structure illuminated holes in an opaque screen represent atoms and different scattering powers can be represented by varying either the size of the holes or the relative exposure times. The photographic scale is chosen so that light waves are diffracted by this "grating" and the intensities of the diffracted beams should be proportional to the observed X-ray intensities if the original structure is correct. By this method the actual calculation of structure factors is avoided until a late stage of the analysis. It is actually possible to recombine the diffracted light waves to give an optical representation of a Fourier synthesis.

(21) **Use of the  $F^2$  Series:** As described in Section 13, the summation of the  $F^2$  series gives a distribution in which peaks represent interatomic vectors. The height of each peak is proportional to the product of the scattering powers of the two atoms involved and the distance of the peak from the origin corresponds to the interatomic distance. Any such map contains a large peak at the origin which expresses the fact that every atom is at zero distance from itself, but it is possible to remove the origin peak artificially. Theoretically, a crystal structure may be deduced from the Patterson diagram but in practice this is not always possible. If there are  $n$  peaks in the corresponding Fourier map there will be  $n(n-1)$  in the Patterson map which in complex structures leads to overlapping of peaks and poor resolution. All the atomic coordinates can be derived from Patterson projections directly only in simple cases and it

<sup>6</sup> W. L. Bragg and H. Lipson, *Z. Krist.*, **95**, 323 (1936).

<sup>7</sup> *Nature*, **154**, 69 (1944).

is these cases which can generally be readily solved by other methods. Three dimensional Patterson functions will, of course, give better resolution and more information than the usual two dimensional projections, but the labor involved is great and the full series has rarely been used.

The most widespread use of the  $F^2$  series up to the present seems to have been in structures where one atom is of much higher atomic number than the

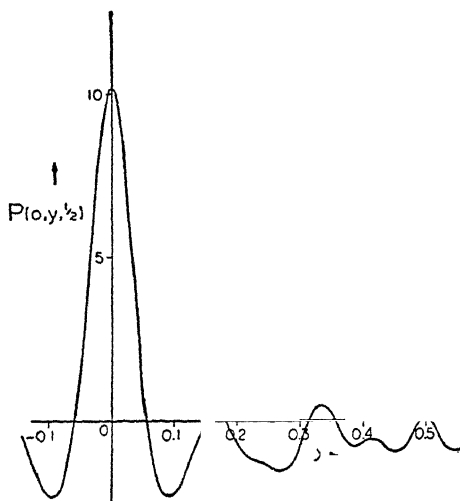


FIG. 39.

aids of various types, three-dimensional Patterson syntheses will be carried out more frequently in the future.

The use of the Patterson-Harker method is well illustrated by the determination of the structure of proustite,  $\text{Ag}_3\text{AsS}_3$ , described by Harker in the original paper on his extension of the Patterson method.<sup>1</sup> The space-group of this crystal is  $R\bar{3}c$ . From symmetry the arsenic atoms must be at the special positions  $(000)$  and  $(00\frac{1}{2})$  and the sulfur and silver atoms in sixfold general positions. The problem reduces to finding six atomic parameters, viz., the  $x$ -,  $y$ - and  $z$ -coordinates for one sulfur atom and for one silver atom. Because of the glide plane perpendicular to  $b$  it is found that the Patterson function will show maxima at  $[0, \pm(x - 2y), \frac{1}{2}]$ ;  $[0, \pm(-2x + y), \frac{1}{2}]$ ;  $[0, \pm(x + y), \frac{1}{2}]$  for each type of atom. Evaluation of the function  $P(0, y, \frac{1}{2})$  therefore gives both  $x$ - and  $y$ -coordinates for each atom.

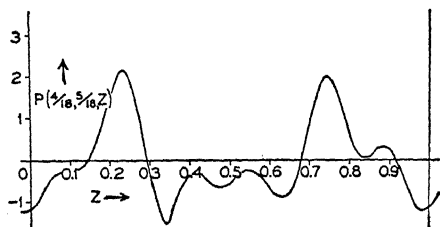


FIG. 40.

<sup>1</sup> D. Harker, *loc. cit.*

The graph of this function is shown in Fig. 39. The large peak at  $y = 0$  is due to the vector between the two arsenic atoms and the other three peaks to silver atomic vectors. The silver parameters can be deduced as  $x = \frac{1}{4}$ ,  $y = \frac{5}{8}$ . The  $z$ -coordinates can then be found by computation of the function  $P(\frac{1}{4}, \frac{5}{8}, z)$ , the result for which is shown in Fig. 40. The two dominant maxima must be due to vectors between the silver and arsenic atoms and the remaining silver coordinate is readily calculated. Harker was not able to find the sulfur position by this direct method as these atoms are relatively light and maxima due to sulfur vectors are insignificant compared with those corresponding to the heavier atoms.

(22) **The Heavy Atom Method:** In a few very specialized cases it is possible to carry out a "direct" X-ray analysis. In the strictest sense this can only be done where the structure contains an atom heavy enough to outweigh the contributions of all other atoms even if they are in phase and the heavy atom must be located at a center of symmetry in the relevant projection of the unit cell. Further, the projection unit cell must contain only one such atom otherwise its contributions would be reduced by the other similar atoms for certain reflections. This only refers to the apparent unit cell in projection, however, and need not necessarily be true of the three dimensional crystal unit cell. Under these conditions all the phase angles for reflections of the zone considered are  $0^\circ$  and a Fourier synthesis can be carried out directly by summing all observed structure amplitudes with positive sign in the appropriate formula. This was first achieved by Robertson and Woodward<sup>1</sup> in the case of platinum phthalocyanine,  $C_{32}H_{16}N_8Pt$ . The Fourier projection map of the (010) plane is shown in Fig. 41 where all atoms except the very light hydrogens are very clearly resolved.

Unfortunately this procedure is possible in very few cases but nevertheless the use of a heavy atom derivative of a complex organic molecule has become the basis of the solution of structures too difficult to solve by other methods. Usually the heavy atom occupies a general crystal position (although a centrosymmetrical projection of the unit cell is almost essential), with the result that it makes little or no contribution to the structure amplitudes of several reflections. The position of this atom can usually be found from a Patterson projection and its contributions to the structure factors of all the reflections in the zone calculated. It is then possible to make a Fourier synthesis using only those reflections whose phase angles are obviously determined by the heavy atom contribution. Probably there will not be sufficient terms in this Fourier series to define all the lighter atoms but the general position of the molecule may appear so that after a stage of trial and error it is possible to elucidate the structure completely.

The crystal structure of cholesteryl iodide has been determined in this way by Carlisle and Crowfoot.<sup>2</sup> This substance crystallizes in the monoclinic space-

<sup>1</sup> *J. Chem. Soc.*, 36 (1940).

<sup>2</sup> *Proc. Roy. Soc.*, A184, 64 (1945).

group  $P2_1$  with two molecules in the unit cell. Although the structure itself has no center of symmetry, the projection on the (010) plane has such a center and the  $x$ - and  $z$ -coordinates of the iodine atoms, which are in general positions, were found accurately from a two-dimensional Patterson synthesis. A Fourier projection map calculated from the observed magnitudes of the struc-

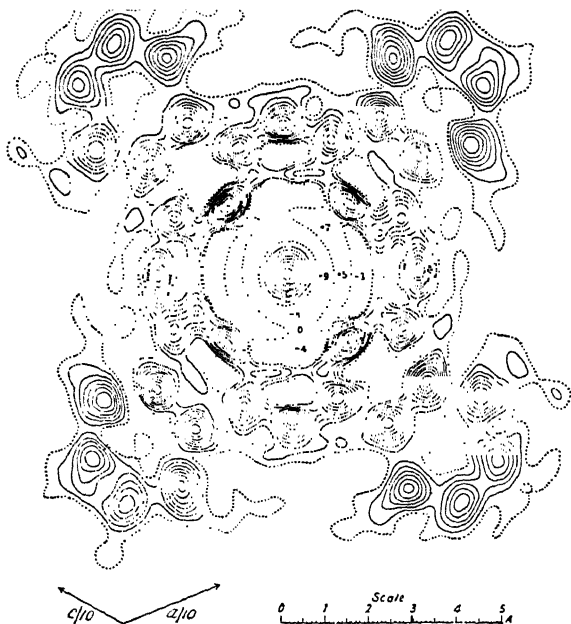


FIG. 41. Electron densities in the  $b$  projection of platinum phthalocyanine (Robertson and Woodward).

ture factors and the phase constants of the iodine atoms, indicated the general outline of the sterol skeleton. The complexity of the structure, however, made the computation of three-dimensional Fourier sections necessary and in this work the phase constants calculated from the iodine positions tended to introduce false symmetry into the structure with the result that spurious peaks of a mirror image of the molecule appeared. However, it was possible to assign all the atomic positions correctly and the geometry of the molecule is established beyond any doubt.

(23) **Use of an Isomorphous Series:** The introduction into an organic molecule of an atom heavy enough to outweigh in scattering power the rest of the molecule combined causes diffraction effects which add false detail to the Fourier projection map and reduces the accuracy of the analysis. Also, as has been pointed out, if the heavy atom is located at a general position in the unit cell, the phase constants of certain reflections will remain indeterminate as

these reflections receive little or no contribution from the heavy atom. Where the method can be applied the use of an isomorphous series is preferable. The general conditions required are the same as those for the simple heavy atom method, and in addition it is necessary for the crystal structure to be unchanged in other respects on substituting one atom for another of different scattering power at the same point in the unit cell.

The method was used by Cork in the determination of alum structure<sup>1</sup> and its first application in organic chemistry was Robertson's direct analysis of the structure of phthalocyanine,<sup>2,3</sup>  $C_{32}H_{18}N_8$ . Phthalocyanine itself and nickel phthalocyanine,  $C_{32}H_{18}N_8Ni$ , both crystallize in the monoclinic space-group  $P2_1/a$  with two molecules per unit cell. The cell dimensions are almost identical in both cases and the nickel atoms must be at symmetry centers. Since the structure is centro-symmetrical the phase angles for all reflections are  $0^\circ$  or  $180^\circ$ . The nickel atom, situated at the origin in nickel phthalocyanine contributes a wave with a peak at the origin to all the  $(h0l)$  reflections. Therefore by comparing the absolute magnitudes of  $F$  for these reflections in the nickel compound and the metal-free compound it is possible to determine the phase constants. If a reflection is of positive phase in phthalocyanine then the absolute intensity of the reflection, corrected by the usual factors, will be much greater in the nickel derivative as the maximum positive nickel contribution cooperates with the resultant wave from the rest of the molecule. If the phase constant is negative then the resultant wave from the lighter atoms interferes with the wave from the nickel atom and the intensity is reduced compared with the previous case. Since the difference in magnitude between the two possibilities is twice the nickel contribution, which is a maximum for every reflection, the phases of almost all the observed  $(h0l)$  reflections for phthalocyanine could be calculated and a Fourier synthesis of these reflections gave very clear resolution of every carbon and nitrogen atom in the molecule.

Where the replaceable atom does not coincide in position with a symmetry center, it is not possible of course to determine all the phase constants desired, but it is clear that several more can be determined than in the comparable case where the simple heavy atom method is used. A very beautiful example is the analysis of sucrose sodium bromide,  $C_{12}H_{22}O_{11}NaBr \cdot 2H_2O$  by Beevers and Cochran.<sup>4</sup> In this structure the bromine atoms occupy general crystal positions. The corresponding sodium chloride compound of sucrose is isomorphous and both belong to the space-group  $P2_12_12_1$  which gives a centro-symmetrical plane group on projection down each of the three crystal axes. The position of the bromine atom was first found accurately from Patterson projections and its contributions to the reflections of the main zones calculated. By a comparison of the absolute intensities of the reflections of both compounds it was then possible to determine a sufficient number of the phase constants to carry

<sup>1</sup> *Phil. Mag.*, **4**, 688 (1927).

<sup>2</sup> *J. Chem. Soc.*, 615 (1935).

<sup>3</sup> *Ibid.*, 1195 (1936).

<sup>4</sup> *Proc. Roy. Soc.*, **A190**, 257 (1947).

out Fourier series projections for the bromide which led to the complete analysis of the structure.

(24) **Anomalous Atomic Scattering:** One method which has not yet been used for structure determination would be rather similar in effect to the isomorphous series technique. The scattering power of an atom is not constant for different X-ray wavelengths but undergoes fluctuations in the critical absorption region. This effect has been carefully studied for nickel by Wyckoff<sup>1</sup>

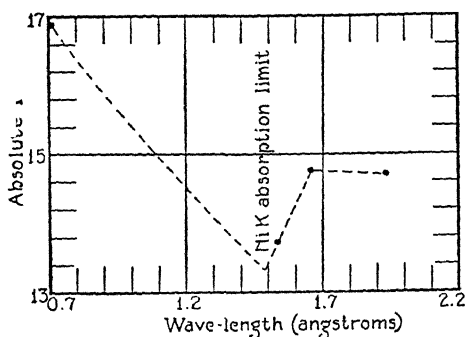


FIG. 42.

and Fig. 42 shows the variation in the atomic scattering power of the nickel atom, for constant  $\sin \theta/\lambda$  over a range of wavelengths. At a wavelength which is distant from an absorption edge the scattering power does not vary much but as the absorption edge is approached from the short-wave side there is a continuous decrease in the absolute magnitude of  $F$ . Near the  $K_{\alpha}$  doublet frequency the scattering power increases sharply and remains at a practically constant value on the long-wave side. It seems quite possible that this physical property could be used for phase determinations. For example, if a nickel atom were combined with an organic molecule then the difference in the absolute values of the structure factors of reflections obtained both with  $\text{Cu } K_{\alpha}$  and with  $\text{Mo } K_{\alpha}$  radiation would be due almost entirely to the change in the scattering power of the nickel atom. Since the nickel atom could be located by Patterson syntheses its absolute contributions to the structure factors of the reflections could be calculated. As the diffracting power of nickel is smaller for copper radiation than for molybdenum an increase in  $F$  on passing from molybdenum to copper would mean that the phase of the resultant wave obtained by compounding the separate waves scattered by all the atoms was opposite to the phase of the wave scattered by the nickel atom alone (assuming a centro-symmetrical crystal). On the other hand a decrease in the absolute intensity would mean that the nickel contribution had probably the same phase as the resultant reflection. A change in the phase of a weak reflection from one experiment to the other, however, might be difficult to identify under experimental conditions.

The data from the two experiments described above for a hypothetical case would be related in exactly the same way as that which would be obtained from two isomorphous crystals which were examined by the same X-ray wavelength. One disadvantage of an isomorphous series is that there are almost always small changes of parameters which can make difficult the calculation of some

<sup>1</sup> *Phys. Rev.*, **36**, 1116 (1930).

phase constants. On the other hand an isomorphous series generally gives a greater change in scattering power for the replaceable atoms than does a change in wavelength. The principal drawback to the use of an absorption edge is the limited number of elements to which the method is easily applicable.

(25) **Application of Inequality Theorems:** Harker and Kasper have recently shown<sup>1</sup> that it is sometimes possible to deduce the phases of X-ray reflections from the absolute magnitudes of the structure factors and certain inequality relations. As shown in Section 11

$$F(hkl) = V \int_0^a \int_0^b \int_0^c p(xyz) e^{2\pi i \left( \frac{hx}{a} + \frac{ky}{b} + \frac{lz}{c} \right)} dx dy dz \quad (25.1)$$

Schwartz's inequality is

$$\left| \int fg dT \right|^2 \leq \left( \int |f|^2 dT \right) \left( \int |g|^2 dT \right) \quad (25.2)$$

and by applying this relation to Equation (25.1)

$$\begin{aligned} |F_{hkl}|^2 &\leq V^2 \left[ \int_0^a \int_0^b \int_0^c \rho(xyz) dx dy dz \right] \\ &\quad \times \left[ \int_0^a \int_0^b \int_0^c \rho(xyz) \left| e^{2\pi i \left( \frac{hx}{a} + \frac{ky}{b} + \frac{lz}{c} \right)} \right|^2 dx dy dz \right] \\ \text{i.e. } |F_{hkl}|^2 &\leq V^2 \left[ \int_0^a \int_0^b \int_0^c \rho(xyz) dx dy dz \right]^2 \quad \text{or} \quad |F_{hkl}|^2 \leq Z^2 \quad (25.3) \end{aligned}$$

where  $Z$  is the total number of electrons per unit cell and  $Z = F(000)$ . The general procedure in setting up inequality relations is to simplify Equation (25.1) by means of a known crystal symmetry relation and then to apply Schwartz's inequality. For example, if there is a center of symmetry at the crystal origin,  $p(xyz) = p(-x - y - z)$  and

$$F_{hkl} = V \int_0^a \int_0^b \int_0^c \rho(x, y, z) \cos 2\pi \left( \frac{hx}{a} + \frac{ky}{b} + \frac{lz}{c} \right) dx dy dz$$

Applying (25.2)

$$\begin{aligned} &\leq V^2 \left[ \int_0^a \int_0^b \int_0^c \rho(xyz) dx dy dz \right] \\ &\quad \times \int_0^a \int_0^b \int_0^c \frac{1}{2} \rho(xyz) \left[ 1 + \cos 2\pi \left( \frac{2hx}{a} + \frac{2ky}{b} + \frac{2lz}{c} \right) \right] dx dy dz \end{aligned}$$

$$\text{or} \quad F_{hkl}^2 \leq Z \left( \frac{1}{2} Z + \frac{1}{2} F_{2h, 2k, 2l} \right)$$

In the Harker and Kasper notation

$$F_{hkl}/Z = \hat{F}_{hkl}$$

<sup>1</sup> *Acta Crystallographica*, 1, 70 (1948).



$$\text{and} \quad \hat{F}_{hkl}^2 \leq \frac{1}{2} + \frac{1}{2} \hat{F}_{2h, 2k, 2l} \quad (25.4)$$

Thus if  $\hat{F}_{hkl}^2$  is greater than  $\frac{1}{2}$ ,  $F_{2h, 2k, 2l}$  must be positive.

Similarly the presence of a two fold rotation axis down  $y$  leads to the inequality

$$|\hat{F}_{hkl}|^2 \leq \frac{1}{2} + \frac{1}{2} \hat{F}_{2h, 0, 2l} \quad (25.5)$$

This sort of relation becomes of practical value when the atomic concept is introduced and the structure factor expression of Section 9 is used

$$F_{hkl} = \sum_{j=1}^N f_j e^{2\pi i \left( \frac{hx_j}{a} + \frac{ky_j}{b} + \frac{lz_j}{c} \right)}$$

$N$  being the total number of atoms and  $f_j$  the atomic scattering factor of the  $j$ th atom. Since atomic scattering curves as a function of  $\sin \theta/\lambda$  are fairly similar provided that the atomic numbers of the different atoms do not differ by a large amount the approximation can be made that  $Z_j \hat{f} = f_j$  where  $\hat{f}$  is the same at constant  $\sin \theta/\lambda$  for every atom.

$$\text{Then} \quad F_{hkl} = \hat{f} \sum_{j=1}^N Z_j e^{2\pi i \left( \frac{hx_j}{a} + \frac{ky_j}{b} + \frac{lz_j}{c} \right)}$$

and it can be seen that this is essentially the same procedure described in Section 9 where a composite scattering curve is used. Now if  $S_{hkl}$  is the geometrical structure factor

$$S_{hkl} = \frac{F_{hkl}}{Z \hat{f}} \quad (25.6)$$

If  $Z_j/Z = n_j$  where  $n_j$  is the fraction of the total number of electrons on the  $j$ th atom.

$$S_{hkl} = \sum_{j=1}^N n_j e^{2\pi i \left( \frac{hx_j}{a} + \frac{ky_j}{b} + \frac{lz_j}{c} \right)} \quad (25.7)$$

Cauchy's inequality is

$$\left| \sum_{j=1}^N a_j b_j \right|^2 \leq \left( \sum_{j=1}^N |a_j|^2 \right) \left( \sum_{j=1}^N |b_j|^2 \right)$$

and can be applied to (25.7) to give

$$|S_{hkl}|^2 \leq 1 \quad \text{since} \quad \sum_{j=1}^N n_j = 1$$

Again we can introduce the effect of a symmetry element. A mirror plane  $xz$ , requires that for an atom at  $x, y, z$ , there is an equivalent atom at  $x, -y, z$  (25.7) becomes

$$S_{hkl} = \sum_{j=1}^{1/2N} n_j e^{2\pi i \left( \frac{hx_j}{a} + \frac{lz_j}{c} \right)} \cos 2\pi \frac{ky_j}{b}$$

and consequently  $|S_{hkl}|^2 \leq \frac{1}{2} + \frac{1}{2} S_{02k0}$ . It can be seen that the use of the atomic form of the structure factor expressions has greatly increased the power of these inequalities as division by  $\hat{f}$  gives  $|S_{hkl}|$  which is greater than the original  $|\hat{F}_{hkl}|$ . It was found that by the type of inequalities discussed above it was only possible to prove the sign of a structure factor to be negative if a glide plane or screw axis is present but the scope was extended by developing inequalities from the sum and difference of two structure factors. By this means Harker and Kasper deduced several phase constants of one zone of reflections in decaborane<sup>2</sup> and were able to complete the structure analysis of this crystal. Gillis<sup>3</sup> has extended the mathematical treatment and has deduced the phases of forty-two reflections of the  $h0l$  zone in oxalic acid dihydrate.<sup>4</sup>

The main weakness of this approach in the general case is that usually the larger the values of  $|S_{hkl}|$  which occur the stronger are the resulting inequalities. In more complex structures the number of reflections having very large values of  $|S_{hkl}|$  is much fewer than in simple structures. The other limitation that the constituent atoms must not differ too widely in atomic number is less serious as a wide range of compounds are included in this category.

#### (26) Expansion of the Crystal:

An ingenious method of phase determination has been used in protein work to which it is peculiarly applicable. In methemoglobin<sup>1</sup> the crystal unit cell of the wet protein expands as successive amounts of water are taken up. The intensities of the  $00l$  reflections were measured for four different states of expansion. The plot of intensity against  $\sin \theta$

is shown in Fig. 43(a). This must always be positive as the intensity is proportional to  $F^2$  but the assumption is that the curve of  $F^2$  falls to zero when  $F$  changes from positive to negative. The numbers in Fig. 43(a) refer to the order of reflection and it can be seen that there are four points at which the  $F^2$  curve seem to touch zero. Fig. 43(b) is the diagram of the  $F$  curve suggested

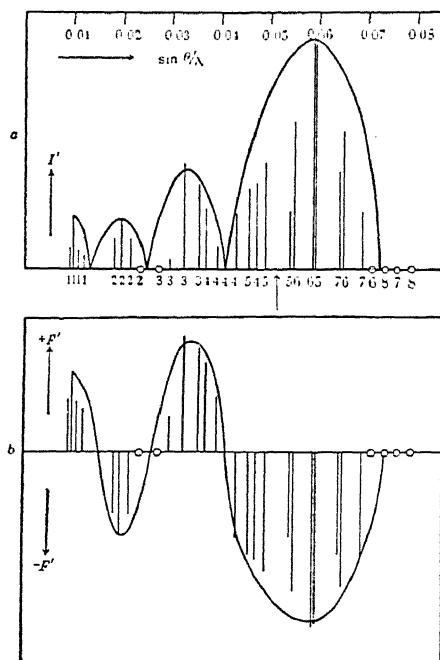


FIG. 43.

<sup>2</sup> To be published.

<sup>3</sup> *Acta Crystallographica*, 1, 76 (1948).

<sup>4</sup> J. M. Robertson and I. Woodward, *J. Chem. Soc.*, 1817 (1936).

<sup>1</sup> J. Boyes-Watson, E. Davidson, and M. F. Perutz, *Proc. Roy. Soc.*, A191, 83 (1947).

by this result and the relative phases (+1 or -1) of most of the orders of reflection can be deduced.

### SOME RESULTS OF X-RAY ANALYSIS OF CRYSTALS

(27) **Potential Energy of Ionic Crystals:** The basic modern theory of ionic crystals is due to Born and Landé,<sup>1</sup> and although modifications have been made the essential arguments remain unchanged. If two ions a distance  $r$  apart have point charges  $z_1e$  and  $z_2e$  then the electrostatic potential energy is

$$u = z_1 z_2 \frac{e^2}{r}$$

In a crystal a repulsive force must operate at small values of  $r$  as the ion pair attains equilibrium at a fixed radius. The energy of an ion pair in a crystal is therefore expressed by a relation of the form

$$u = z_1 z_2 \frac{e^2}{r} + \frac{b}{r^n}$$

However, every ion pair is affected by the electrostatic field of every other ion pair and a geometrical correction factor is necessary, from which

$$u = A z_1 z_2 \frac{e^2}{r} + \frac{B}{r^n} \quad (27.1)$$

The first term is negative for oppositely charged ions and the second term positive.  $A$  is the Madelung constant which has been calculated in very simple cases.<sup>2,3</sup> The power  $n$  in the second term can be calculated both directly on theoretical grounds and also from the observed compressibilities of crystals which are obviously dependent on the repulsive force between ions. For the alkali halides  $n$  is deduced as 9 from compressibility experiments, and calculated theoretically to be 5. The contribution of the second term to the total energy is small, however, and  $u$  is not very sensitive to small changes in the value of  $n$ .

For the alkali halides

$$u = -\frac{Ae^2}{r} + \frac{B}{r^n} \quad (27.2)$$

$B$  can be found in terms of  $A$  since at the equilibrium radius  $r_0$  the crystal potential energy is a minimum. Thus

$$\left( \frac{\partial u}{\partial r} \right)_{r=r_0} = \frac{Ae^2}{r^2} - \frac{nB}{r^{n+1}} = 0$$

$$B = \frac{Ae^2 r_0^{n-1}}{n}$$

<sup>1</sup> *Verh. deutsch. phys. Ges.*, 20, 210 (1918).

<sup>2</sup> E. Madelung, *Z. Physik*, 19, 524 (1918).

<sup>3</sup> P. P. Ewald, *Ann. Physik*, 64, 253 (1921).

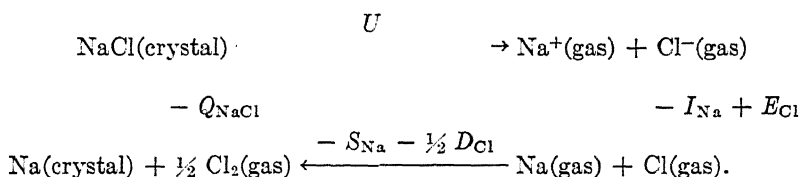
and

$$u = -\frac{Ae^2}{r_0} \left(1 - \frac{1}{n}\right)$$

For one gram molecule the energy  $U = Nu$ , therefore

$$U = -\frac{NAe^2}{r_0} \left(1 - \frac{1}{n}\right) \quad (27.3)$$

The crystal energy  $U$  obtained from Equation (27.3) can be correlated with known thermochemical quantities, in order to test the underlying theory, by means of the Born-Haber cycle:



Taking sodium chloride as an example  $I_{\text{Na}}$  is the energy of ionization of sodium gas and  $E_{\text{Cl}}$  the electron affinity of atomic chlorine gas.  $S_{\text{Na}} + \frac{1}{2}D_{\text{Cl}}$  is obtained from the system on forming metallic sodium and molecular chlorine, where  $S_{\text{Na}}$  is the heat of sublimation of metallic sodium and  $D_{\text{Cl}}$  the energy of dissociation of molecular chlorine. On chemical combination of sodium and chlorine  $Q_{\text{NaCl}}$ , the heat of formation of sodium chloride is recovered. The total energy change is zero when one gram molecule is passed through the complete cycle, therefore

$$U_{\text{NaCl}} - I_{\text{Na}} + E_{\text{Cl}} - S_{\text{Na}} - \frac{1}{2}D_{\text{Cl}} - Q_{\text{NaCl}} = 0 \quad (27.4)$$

All quantities in Equation (27.4) are measurable except  $U$  and  $E$ . The original method adopted was to use the calculated values of  $U$  for a series of different alkali metals combined with the same halogen and to calculate  $E$  for that halogen.  $E$  was found to be constant to about  $\pm 3$  per cent.<sup>4</sup>

Although self-consistent results were obtained for the alkali halides using the Born-Landé theory, in some other crystals the results were less satisfactory. The principal difficulties seemed to be the uncertainty of the magnitude of  $n$  in the term expressing the repulsive ionic interaction and the complete neglect of van der Waals forces. Born and Mayer<sup>5</sup> extended the theory and now wrote Equation (27.2) as

$$u = -\frac{Ae^2}{r} + Be^{-\frac{r}{\rho}} - \frac{c}{r^6} + \epsilon \quad (27.5)$$

The second term in Equation (27.2) is replaced by the exponential term in which the constant  $p$  is again determined from compressibility measurements and

<sup>4</sup> J. Sherman, *Chem. Rev.*, 11, 93 (1932).

<sup>5</sup> Z. *Physik*, 75, 1 (1932).

does not vary much within the alkali halide group. The third term in Equation (27.5) takes account of the van der Waals force the quantum mechanical treatment of which had been developed by London<sup>6</sup> and others.  $\epsilon$  is the zero-point energy contribution and is generally extremely small for ionic crystals, but the van der Waals contribution may be important.

The calculated crystal energy can be used to explain certain physical properties such as melting-points and relative stability of different crystals, but only in one or two very simple cases is it possible to answer by a purely mathematical treatment the very important question of why a substance crystallizes in a certain structure and not in another. For a given substance the calculated crystal potential energies for two conceivable structures differ by only a very small fraction of the total potential energy and the theory has not attained such precision that differences of this order of magnitude in the calculated potential energies are necessarily real. However, it is sometimes possible to find out whether assumptions about the type of bonding in a crystal are essentially correct as here two radically different hypotheses may give relatively large differences in the calculated values of the crystal potential energy.

(28) **Ionic Bond Radii and Structural Principles:** The X-ray measurements on ionic crystals give values of the equilibrium distances between the center of the anions and cations. There is no absolute criterion of the size of an individual cation or anion since the electron distribution is no longer regarded as being discontinuous, but it is a great advantage in structural chemistry to be able to use effective ionic radii such that the anion and cation radii added together give the observed anion-cation crystal distance, and ideally the effective radius for a certain ion should be constant in all ionic structures containing that ion. In order to use the wealth of available X-ray measurements or inter-ionic distances it is necessary to determine at least one ionic radius by an independent method.

Wasastjerna<sup>1</sup> considered that the ionic volume is approximately proportional to the molar refractivity of the ion and on this basis calculated the ratio in which lithium halide interionic distances must be divided in order to give the ionic radii, which he then deduced for several ions. Goldschmidt<sup>2</sup> made a careful survey of ionic crystals and, starting from the radii 1.32 Å for  $O^{2-}$  and 1.33 Å for  $F^{-}$ , tabulated values for more than 80 ions. A more theoretical approach was made by Pauling<sup>3</sup> who took as standard ionic crystals NaF, KCl, RbBr and CsI. For a pair of isoelectric ions the radii may be regarded as being inversely proportional to the effective charges on the respective nuclei, i.e., the nuclear charges corrected for the screening effect of the outer electrons. Pauling thus obtained absolute radii for the alkali metal and halogen ions, and extended the method to other ions, obtaining not absolute radii but "univalent

<sup>6</sup> *Z. Physik. Chem.*, B11, 222 (1930). See this volume, p. 295.

<sup>1</sup> *Soc. Sci. Fennica, Commentationes Phys. Math.*, 38, 1 (1923).

<sup>2</sup> *Geochemische Verteilungsgesetze der Elemente, Skrifter Norske Videnskaps-Akad. Oslo. I. Mat.-Naturv. Klasse* (1926).

<sup>3</sup> *J. Am. Chem. Soc.*, 49, 765 (1927).

ionic radii." The "univalent radius" of an ion is the radius which the ion would have if it had unit nuclear charge but maintained its electronic structure and Pauling derived appropriate formulae for converting this quantity to the crystal ionic radius. Goldschmidt's radii and Pauling's are in general in good agreement.

The picture of an ion as spherical and of constant radius is, of course, not strictly correct and it can readily be seen that there is more likely to be an approximation to spherical symmetry in a high coordination structure than one of low coordination. In low coordination structures, polarization, or distortion of the electronic structure of an ion by the field of its neighbors, becomes important. However, the relative changes in ionic radii on changing from one type of coordination to another are fairly predictable. Ionic radii are usually quoted in terms of the sodium chloride structure (six-fold coordination) and corrections can be applied for other structure types.

Ionic crystal radii are of course very different from the radii of the corresponding neutral atoms as the loss of extranuclear electrons decreases the effective radius for a positive ion while the additional electrons in the negative ion orbitals increases the radius. This effect is accentuated for a positive ion and lessened for a negative ion by increased attraction between the ion pair. When we compare ions of varying charge which have the same extranuclear electronic structure the radius decreases very rapidly with increasing charge for positive ions but, in the case of negative ions, there is very little change as increased attraction approximately cancels the effect of increased charge.

If an anion X of charge  $-z$  is surrounded by  $n$  neighboring cations so that all the bonds are equivalent then the strength of each bond is defined as  $z/n$ . Now if the anion is coordinated to different cations A, B, C, etc., a bond between X and A of strength greater than  $\frac{1}{2}z$  means that X is attached more strongly to A than to all the other cations. This criterion gives a convenient classification of ionic structures into:

- (1) *Isodesmic structures.* No single anion-cation bond is equal to or greater than  $\frac{1}{2}z$ . This does not mean that all such bonds are equivalent but that there are no discrete groups formed within the structure.
- (2) *Mesodesmic structures.* A cation-anion bond is  $\frac{1}{2}z$  and therefore equal in strength to all other bonds to the anion. The silicates, the most important structures in this class, will be discussed in Section 29.
- (3) *Anisodesmic structures.* A bond from the anion to one cation is greater than  $\frac{1}{2}z$  and therefore stronger than all other bonds from the anion. Strongly bound groups such as nitrate, chlorate, etc., may actually persist in solution when the other crystal bonds have been broken.

Isodesmic structures are further divided into simple where there is only one cation, and multiple where there are two or more cations.

The most important factors determining the structures of simple isodesmic ionic crystals are:

- (1) Ionic radii.
- (2) Polarizability of the ions.
- (3) Polarizing power of the ions.

Where a cation is surrounded by anions of the same kind we may expect that the structure will be unstable if the radius ratio of anion to cation is such that the anions cannot be in contact with the cations. Obviously the potential

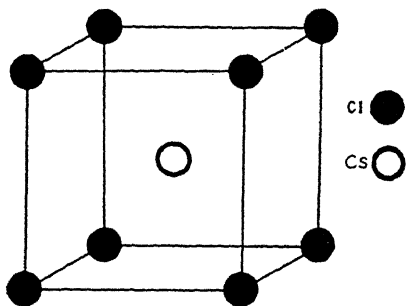


FIG. 44.

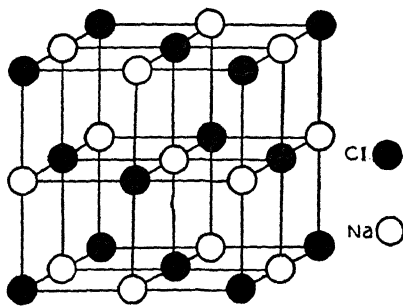


FIG. 45.

energy of the crystal is not a minimum and the type of coordination will change to one where the cation can be in contact with all the surrounding anions. The limits of the radius ratio for different coordination numbers are readily calculated.

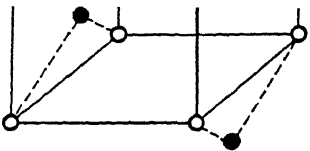
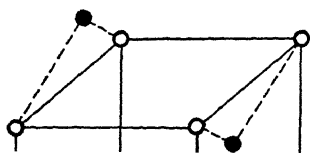


FIG. 46.

For example, if  $R_A:R_X > 0.732$  we should expect the caesium chloride type of structure (Fig. 44) with eightfold coordination to be stable, while, if the ratio falls just below this limit, the coordination number should change to 6 and we should expect the sodium chloride structure type to be stable (Fig. 45). There is a general agreement between observed structure types and those predicted on this simple geometrical principle but there are exceptions. This is easily explained when we remember that the difference in crystal energy between the two coordination types may be extremely small and factors not taken into account may cause the critical difference.

Polarizability becomes more important the greater the size of the ion and hence the effect is much more drastic with anions than with cations. The polarizing power of an ion is greatest when the ionic charge is high and the

radius is small. Goldschmidt has used  $Ze/r^2$  as a measure of polarizing power. Polarization in ionic crystals has the effect of tending to change the binding away from ionic character, although in most cases this is not realized to a large extent. An interesting example of a structure where polarization is important is that of  $\text{CdI}_2$  (Fig. 46). This crystal has a layer type of structure which may be regarded as being intermediate between a true ionic structure and a molecular structure.

With anisodesmic structures, and complex ionic structures in general, an understanding of the general principles of their construction may be obtained by application of the five rules put forward by Pauling.<sup>4</sup> These rules also apply to the simpler structures already discussed but here their application is obvious. Pauling's rules are:

- (1) A coordinated polyhedron of anions is formed about each cation, the cation-anion distance being determined by the radius sum and the coordination number of the cation by the radius ratio.
- (2) In a stable coordination structure the total strength of the valence bonds which reach an anion from all the neighboring cations is equal to the charge of the anion. In other words, this rule states that there is a local neutralization of charge throughout the crystal.
- (3) The existence of edges, and particularly of faces, common to two anion polyhedra in a coordinated structure decreases its stability; this effect is large for cations with high valence and small coordination number, and is especially large when the radius ratio approaches the lower limit of stability of the polyhedron.
- (4) If a crystal contains different cations those of high valence and small coordination number tend not to share polyhedron elements with each other.
- (5) The number of essentially different kinds of constituents in a crystal tends to be small.

(29) **The Structure of the Silicates:**<sup>1</sup> The basis of silicate structures is the tetrahedral coordination of four  $\text{O}^{2-}$  ions around one  $\text{Si}^{4+}$  ion. Since the anion is much larger than the cations commonly found in silicates the simpler structures, at least, consist of a close-packed assembly of oxygen ions with the silicon and other cations fitting into the interstices in such a manner as to achieve the appropriate coordination. The silicates may be classified according to the method of sharing of oxygen ions by the silicon ions as follows:

- (1) Structures with discrete anions.
  - (a) Orthosilicates,  $\text{SiO}_4^{4-}$
  - (b)  $\text{Si}_2\text{O}_7^{6-}$ ,  $\text{Si}_3\text{O}_9^{6-}$ ,  $\text{Si}_6\text{O}_{18}^{12-}$
- (2) Chains formed by linking  $\text{SiO}_4$  tetrahedra,  $\text{SiO}_3^{2-}$ ,  $\text{Si}_4\text{O}_{11}^{6-}$
- (3) Sheets formed by cross-linking chains,  $\text{Si}_2\text{O}_5^{2-}$

<sup>4</sup> *J. Am. Chem. Soc.*, **51**, 1010 (1929).

<sup>1</sup> W. L. Bragg, *Atomic Structure of Minerals* (New York: Oxford University Press, 1937).



(4) Three-dimensional networks formed by cross-linking sheets. The structural types 1-3 are shown diagrammatically in Fig. 47.

One of the most important orthosilicates is olivine  $(\text{Mg, Fe})_2\text{SiO}_4$ . The coordination number of  $\text{Mg}^{2+}$  is 6 so that the magnesium ions are situated among the  $\text{SiO}_4^{4-}$  tetrahedra in such a way that each magnesium is surrounded by six oxygens. Each oxygen is then linked to one silicon and three mag-

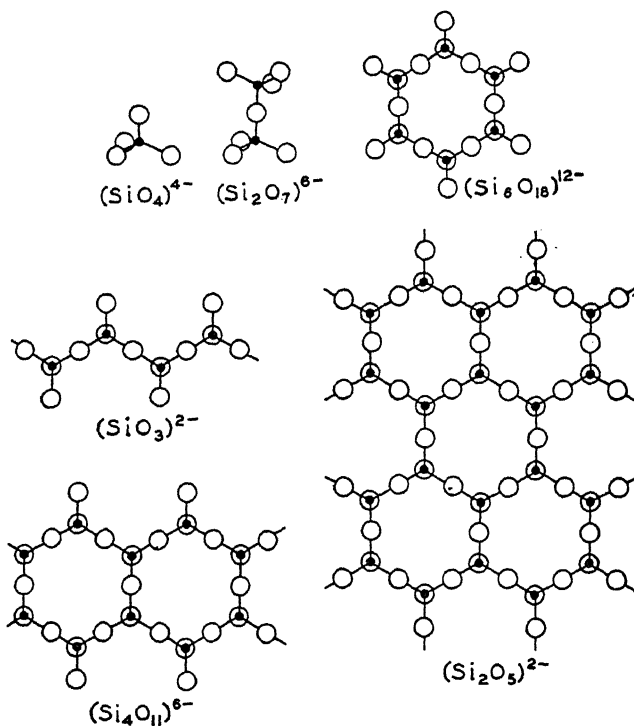


FIG. 47.

nesiums. Pauling's second rule may be illustrated by considering one oxygen ion. The strength of each electrostatic bond from magnesium to oxygen is  $\frac{2}{6} = \frac{1}{3}$  and three such bonds are directed to each oxygen atom giving a total of +1. Each silicon-oxygen bond is of strength  $+\frac{4}{4} = +1$  so that all the oxygen bonding gives a net charge of +2 which neutralizes locally the charge on the  $\text{O}^{2-}$  ion. Beryllium and zinc have fourfold oxygen coordination. In the structures phenacite,  $\text{Be}_2\text{SiO}_4$  and willemite  $\text{Zn}_2\text{SiO}_4$  each oxygen atom is shared between one silicon tetrahedron and two zinc or beryllium tetrahedra. A very interesting example of the ring type of discrete anion is beryl,  $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ , shown in Fig. 48. The  $\text{SiO}_4$  groups are drawn as tetrahedra and the aluminum and beryllium atoms are indicated separately. Each beryllium

is in tetrahedral coordination with oxygens from four different rings and each aluminum is coordinated octahedrally with oxygens from six different rings.

The extended chain type of structure is found in the pyroxenes and amphiboles. The simplest of the pyroxenes is diopside,  $\text{CaMg}(\text{SiO}_3)_2$ . The basic silicate chain is formed by sharing one oxygen between two tetrahedra and the vertices of the tetrahedra point in opposite directions in successive members of the chain. The chains are linked together by cations, the magnesium ion in sixfold and the calcium ion in eightfold coordination. The amphiboles contain a double pyroxene chain which may be regarded as an indefinite extension in

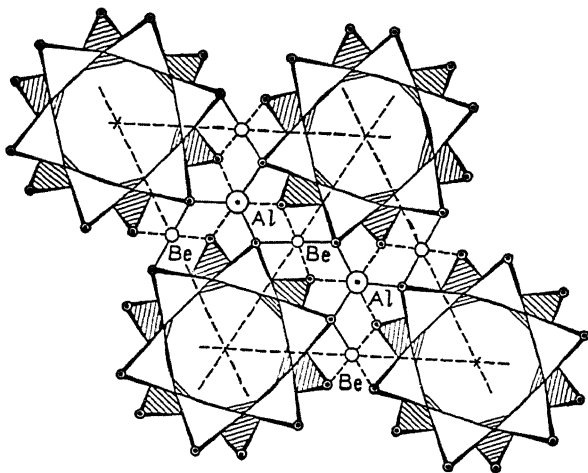


FIG. 48. The structure of beryl,  $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ .

one dimension of the six-membered ring of  $\text{SiO}_4$  tetrahedra found in beryl. Amphiboles are generally more complex than pyroxenes and contain either hydroxyl or fluorine ions, e.g., tremolite,  $(\text{OH}, \text{F})_2\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{23}$ . The fibrous structure of these materials is due to the stronger silicon-oxygen linkages within the chains compared with the cross-linkages through cations.

The sheetlike structures are formed by an indefinite extension of the six-membered ring in two dimensions, with cross linkages through cations between successive sheets. However here, as is the case in some chain structures, great complexity may arise because of isomorphous substitution, and in particular from the presence of aluminum. The  $\text{Al}:\text{O}$  ionic radius ratio is extremely close to the critical value at which transition from sixfold to fourfold coordination takes place, so that the aluminum ion occurs in both conditions and may do so within the same structure. Fourfold coordinated aluminum replaces  $\text{Si}^{4+}$  and since this leads to a local negative charge there must be a substitution of  $\text{Ca}^{2+}$  for  $\text{Na}^+$ ,  $\text{Al}^{3+}$  for  $\text{Mg}^{2+}$  or  $\text{Fe}^{3+}$  for  $\text{Fe}^{2+}$  at some point in the structure for every silicon ion replaced in this manner, in order to preserve electrical neutrality. Replacement of one cation by another between the  $\text{Si}_2\text{O}_5^{2-}$  sheets is illustrated

in Fig. 49 where projections of the structures of talc,  $3\text{MgO} \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$  and pyrophyllite,  $\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$  are made normal to the sheet planes.<sup>2</sup> Six  $\text{Mg}^{2+}$  ions in talc are replaced by four  $\text{Al}^{3+}$  ions in pyrophyllite, electrical neu-

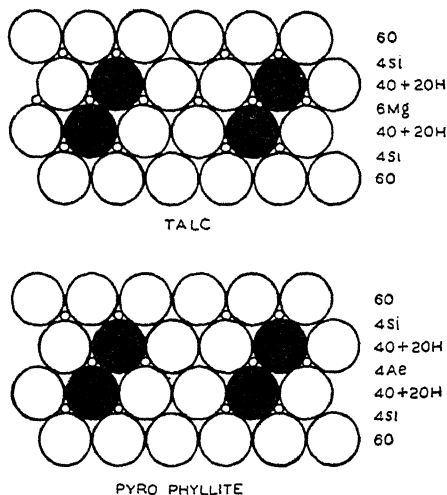


FIG. 49.

trality being preserved. In phlogopite,  $\text{K}_2\text{O} \cdot 6\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot \text{H}_2\text{O}$  each layer has an ionic charge due to replacement of  $\text{Si}^{4+}$  by  $\text{Al}^{3+}$  and the charge is balanced by the presence of alkali metal ions between the layers giving a tighter binding of the whole structure. The cleavage in this type of structure, which includes muscovite, is less marked than in the soft talc group.

(30) **Metals and Alloys:** Metals may be divided into two groups, the true metals which include the alkali and alkaline earth metals and the transition metals, and the *B* subgroup metals which chemically have less basic character than the true metals. Most of the true metals,

with the important exception of Mn, have simple structures of three types:

- $A_1$ . Cubic close-packing.
- $A_2$ . Cubic body-centered structure.
- $A_3$ . Hexagonal close-packing.

Cubic and hexagonal close-packing can be visualized from Fig. 50. There is only one way of making a single close-packed sheet of equal spheres as shown by the full circles. When one such sheet is superimposed on another, one obvious staggered arrangement is that shown by the dotted circles in Fig. 50. However, when a third sheet is placed over these two, there are two possibilities. Either the spheres in the third sheet are directly above those in the first sheet, giving the  $A_1$  structure, or they are in the staggered position not directly above the spheres of either the first or second sheets. This second alternative is the  $A_3$  type structure or hexagonal close-packing. The cubic body-centered type of structure ( $A_2$ ) has been described for ionic crystals. Here each sphere is in

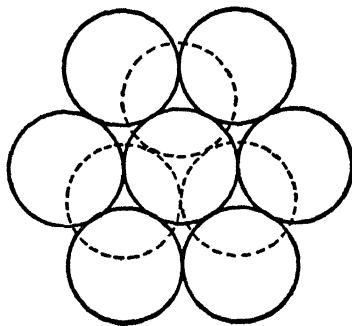


FIG. 50.

<sup>2</sup> L. Pauling, *Proc. Nat. Acad. Sci.*, 14, 603 (1928).

contact with eight neighbors. In both the close-packed structures each sphere is in contact with twelve neighbors. One important difference between the cubic and hexagonal close-packed arrangements is the number of directions normal to which the sheets are close-packed. In the  $A_1$  type there are four such directions and in the  $A_3$  type only one. Since malleability of metals is due to the gliding of planes over each other this property is most evident with metals which crystallize in the cubic close-packed arrangement, e.g., Cu, Ag, Au, Ni,  $\alpha$ -Co and  $\gamma$ -Fe.

The  $B$  sub-group metals have structures which are more complex than those of true metals and are in fact intermediate between the metallic type of structure and molecular structures. Thus selenium and tellurium crystals have structures which consist of indefinitely extended spiral chains of atoms with much stronger bonds between successive atoms in a chain than between different chains. This arrangement is much more like the fibrous structure of plastic sulfur than any true metal structure. Cadmium and zinc, however, have structures very like those of true metals with an approximation to hexagonal close-packing. For each atom six of its twelve neighbors are rather closer than the other six indicating a slight tendency in the direction of a molecular structure.

Alloys are divided by Evans<sup>1</sup> into four main types: (1) Alloys of two true metals; (2) Alloys of one true metal and one  $B$  sub-group metal; (3) alloys of two  $B$  sub-group metals; and (4) interstitial structures. In group (1) the most extensively investigated system is that of Cu-Au. Both metals crystallize in the close-packed cubic structure and the radius of the copper atom is only slightly smaller than that of the gold atom. If we take pure gold and add copper gradually it is found that substitution in the lattice takes place at random throughout the whole range. A solid solution is formed and the cell dimensions contract as more of the smaller copper atoms are introduced. If, however, the alloy is carefully annealed after each addition of copper, the original random substitution becomes more ordered as more copper is added and when there are an equal number of Cu and Au atoms present the ordered structure shown in Fig. 51 is obtained. Addition of more copper gives at first random replacement but a different ordered structure is found when the composition reaches the proportion of 3 Cu to 1 Au. Further replacement gives eventually the structure of pure copper. Such an ordered arrangement as the Cu-Au phase where the basic structure is the same as for the solid solution, but in which atoms of each kind are arranged regularly is called a "super-

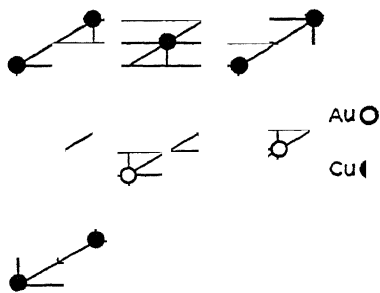


FIG. 51.

<sup>1</sup> *Crystal Chemistry* (London: Cambridge University Press, 1939).

lattice." The order-disorder transformation has been investigated theoretically by W. L. Bragg and Williams<sup>2, 3</sup> who calculated a critical temperature above which all order disappears and the superlattice changes into a solid solution. This theory accounts for the abrupt changes of specific heat with temperature in binary alloys.

The alloy systems formed between true metals and *B* sub-group metals are very complex. There is a greater tendency towards definite chemical attachment than in the case of the true metals. One important group of these alloys is that formed between the transition metals and the more basic of the *B* sub-group metals. Characteristic of this group are the smaller tendency to form solid solutions as compared with true metal alloys and the very common occurrence of three ordered phases known as the  $\beta$ ,  $\gamma$  and  $\epsilon$  phases. The composition of these phases shows no relation to the ordinary laws of chemical combination and it was Hume-Rothery<sup>4</sup> who put forward empirically the rule that the deciding factor is the ratio of the total number of valence electrons in the system to the number of atoms. For the  $\beta$ ,  $\gamma$  and  $\epsilon$  phases, respectively, this ratio is 3:2 (or 21:14), 21:13 and 7:4 (or 21:12). Thus, the composition of the  $\beta$ ,  $\gamma$  and  $\epsilon$  phases of the Cu-Zn system is represented by CuZn, Cu<sub>5</sub>Zn<sub>8</sub> and CuZn<sub>3</sub>.

Interstitial compounds are alloys formed between the transition metals and hydrogen, boron, carbon or nitrogen. The dominant feature of these structures is the small size of the non-metallic atom which usually fits into the holes in a close-packed assembly of the metal atoms. The principle of achieving maximum coordination is fulfilled as far as possible, the non-metal atom fitting into the largest space in which it can be in contact with all the neighboring metal atoms. Thus, the radius ratio of metal to non-metal is critical in determining the exact structure adopted.

The early theory of metals was due to Drude and Lorentz. The metal structure was pictured as an ionic structure in which the charge on the metallic cations was counterbalanced by the negative charge of the electrons. The electrons, however, were not localized but were free to move throughout the crystal in this way giving to metals the property of high conductivity. If the electron is entirely free in its motion then the energy  $E = k^2/2m$  where  $k$  is the momentum of the electron and the proportionality of energy to the square of the momentum is a continuous function. Later developments of the theory<sup>5</sup> expressed the fact that the electron actually moves under a periodic field within a crystal and this gives discontinuities in the energy-momentum curve. Below such a discontinuity the energy is abnormally high, and consequently there are in general certain forbidden regions. In the crystal the electrons are distributed among the "Brillouin zones" of energy and the shape of these zones is a function of the crystal lattice. Under certain condition, therefore, two zones may over-

<sup>2</sup> *Proc. Roy. Soc.*, A106, 369 (1934).

<sup>3</sup> *Proc. Roy. Soc.*, A151, 540 (1935).

<sup>4</sup> *J. Inst. Metals*, 35, 295 (1926).

<sup>5</sup> F. Bloch, *Z. Physik*, 52, 555 (1929).

lap and the forbidden regions disappear. As a metal lattice contracts the zones expand and overlap and the metal develops a high conductivity.

This concept can be used to explain Hume-Rothery's rule of alloy formation. A stable alloy phase may be regarded as one in which the Brillouin zones which contain electrons are filled and there are no zones only partially filled. Calculations of the number of electrons required to fulfill this condition for actual alloy phases give results very close to the empirical electron-atom ratios of Hume-Rothery.

(31) **Molecular Configuration:** From the discussion of ionic structures it is clear that the classical ideas of a chemical compound and of a molecule of substances like sodium chloride have little meaning in the crystalline state.

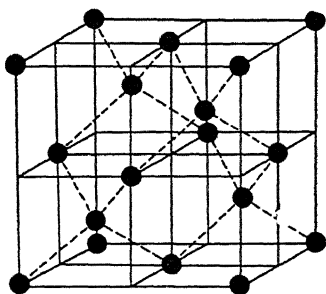


FIG. 52.

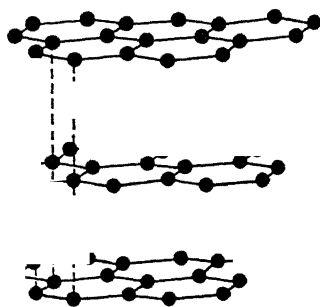


FIG. 53.

The building units of the crystal structure are ions, not molecules and the method of arrangement of the positive and negative ions gives a complete picture of the solid. In molecular structures, however, the building units are molecules and X-ray analysis of a molecular structure can therefore give information of two kinds: the method by which the molecules are packed together to form the crystal and the detailed configuration of the molecule itself.

The allotropy of carbon was understood at an early stage of structure analysis. Diamond<sup>1</sup> has the structure shown in Fig. 52. Each carbon atom is at the center of a tetrahedron with its four neighbors at the vertices. The extension of this system continues throughout the crystal which may therefore be regarded as a giant three-dimensional molecule. A diamond crystal can only be cleaved by breaking a large number of covalent bonds which explains the hardness of the substance. Graphite<sup>2</sup> has a layer structure shown in Fig. 53. In one sheet the carbon atoms are arranged at the points of a regular hexagonal network which extends indefinitely in two dimensions. Alternate sheets have their atoms directly superposed while the atoms of one sheet are in staggered positions relative to the atoms of the next sheet. The distance between successive sheets is 3.41 Å which is much greater than the carbon-

<sup>1</sup> W. H. Bragg and W. L. Bragg, *Proc. Roy. Soc.*, A89, 277 (1913).

<sup>2</sup> J. D. Bernal, *Proc. Roy. Soc.*, A106, 749 (1924).

carbon distances ( $1.42 \text{ \AA}$ ) within each sheet. Graphite consists of a series of two-dimensional giant molecules held together only by very weak forces which give the substance its characteristic physical properties. The stable allotrope of sulfur the orthorhombic modification<sup>3</sup> was shown to have molecules of a puckered ring type illustrated in Fig. 54. The molecules contain eight atoms and the sulfur bond angles are  $105^\circ$  which is constant round the ring.

In organic structures, early work showed that the tetrahedral valence of carbon, predicted by organic chemists and established for diamond, extended to aliphatic compounds. The regular, planar, hexagonal benzene ring, again predicted before the discovery of X-ray diffraction was shown to be a physical reality in many simple aromatic compounds. For many years therefore, as far as the broad structural features of organic compounds were concerned, X-ray analysis achieved little beyond establishing the essential structures de-

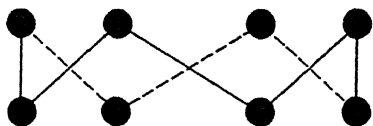


FIG. 54.

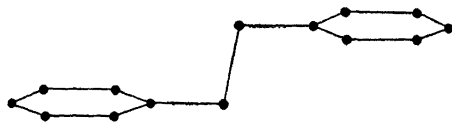


FIG. 55.

duced from organic chemistry. The finer structural details, however, such as the actual bond distances and bond angles discussed in Section 32 could not have been measured by any other method for many of these compounds. Also, in cases where the organic chemical formula allowed structural degrees of freedom such as free rotation about a single bond, the X-ray method gave an exact picture of the molecular geometry in the crystal. For example, dibenzyl<sup>4</sup> was found to have the configuration shown in Fig. 55 with the benzene rings parallel but not coplanar.

In the field of more complex organic molecules it has been shown that a complete X-ray analysis may be extremely difficult and the early method of attack on crystals where the molecular structure was unknown from the organic chemists' point of view, or not completely established, took the form of an extensive survey of a series of chemically closely related structures. From the cell dimensions, symmetry, optical properties and other physical measurements it was sometimes possible to draw conclusions about the shapes of molecules. Two such surveys may be mentioned. Cox, Goodwin and Wagstaff<sup>5</sup> examined over 60 sugars and suggested a flat structure for the pyranose ring although the later structure determination of glucosamine hydrochloride showed the ring to be of the Sachse *trans*-form in this compound. Bernal<sup>6, 7</sup> made a comprehen-

<sup>3</sup> B. E. Warren and J. T. Burwell, *J. Chem. Phys.*, **3**, 6 (1935).

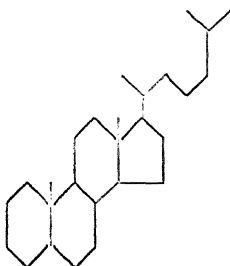
<sup>4</sup> J. M. Robertson, *Proc. Roy. Soc.*, **A150**, 348 (1935); G. A. Jeffrey, *Nature*, **156**, 82 (1945).

<sup>5</sup> *J. Chem. Soc.*, 978 (1935).

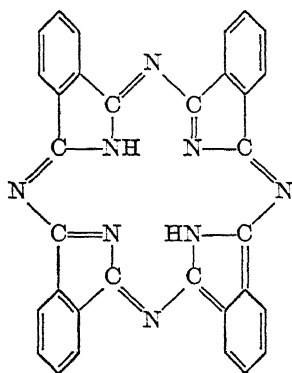
<sup>6</sup> *Nature*, **189**, 277 (1932).

<sup>7</sup> *Nature*, **129**, 721 (1932).

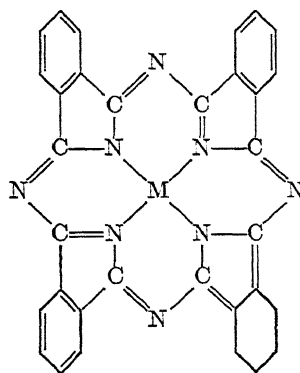
sive survey of the sterols which played a decisive part in the formulation of the structure V for the sterol skeleton.



In the last few years it has been possible to make detailed X-ray analyses of certain complex organic molecules which establish their structure conclusively. This development is certain to be of increasing importance in the future as, under favorable conditions, the X-ray method will be used to shorten considerably the work of the structural organic chemist. The first analysis of a very complex structure, that of phthalocyanine, has been described as an example of the use of an isomorphous series in structure analysis. The result of Robertson's analysis establishes VI as the structure of phthalocyanine in accordance with that suggested by Linstead.<sup>8</sup> The metal derivatives in the series are



VI



VII

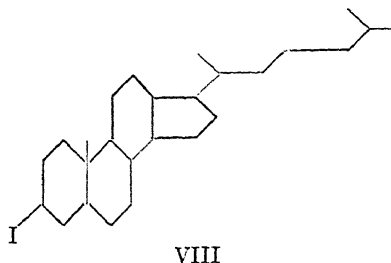
formed by coordination of a metal atom in the center of the molecule in place of two hydrogens (VII) leaving the rest of the molecule practically unchanged. The analysis of cholesteryl iodide (VIII) by Carlisle and Crowfoot<sup>9</sup> gives detailed and conclusive support to the accepted structure of the sterol skeleton.

<sup>8</sup> *J. Chem. Soc.*, 1016 (1934).

<sup>9</sup> *Proc. Roy. Soc.*, A184, 64 (1945).



In recent work, Crowfoot and Dunitz<sup>10</sup> have completed a two-dimensional



Fourier projection of the *p*-iodonitrobenzoyl derivative of calciferol (IX) giving a very clear picture of the molecule which settles decisively the controversy over the structure of this compound.

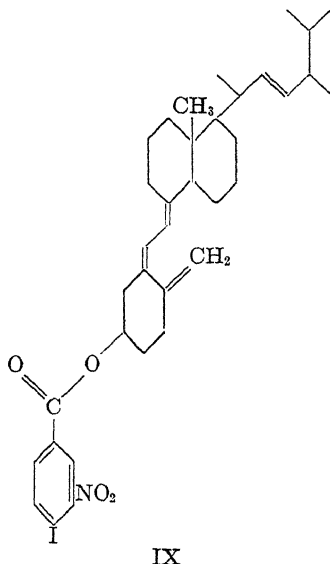
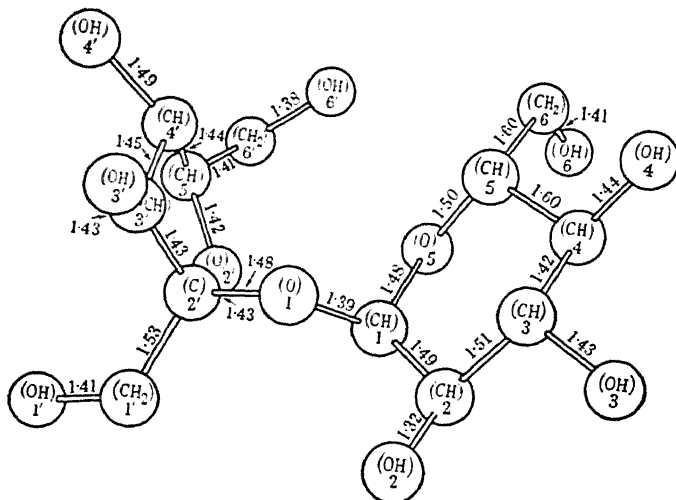


Figure 56 shows the geometry of the sucrose molecule from the X-ray analysis of sucrose sodium bromide dihydrate.<sup>11</sup> The pyranose ring is of the Sachse *trans*-form and contrary to previous hypotheses the atoms of the furanose ring are definitely not coplanar, one member, C4' being about 0.5 Å out of the plane of the other four, a distance which is many times larger than the possible experimental error.

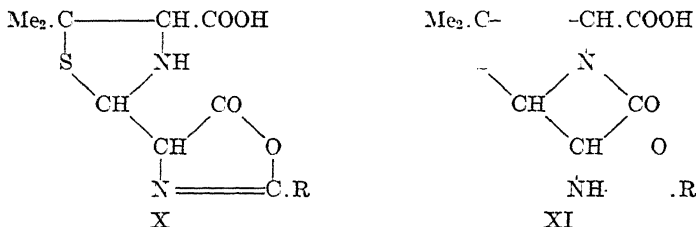
Possibly the most striking example of the power of the X-ray method is the determination of the structure of penicillin by complete X-ray analysis of

<sup>10</sup> *Nature*, **162**, 608 (1948).

<sup>11</sup> Beevers and Cochran, *loc. cit.*



alkali metal salts,<sup>12</sup> well in advance of straightforward chemical structural analysis. This work proved that penicillin has the beta-lactam structure (XI) and not the azlactone structure (X) which had been suggested.

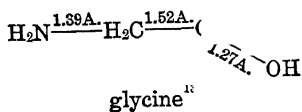
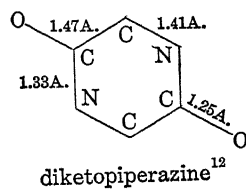
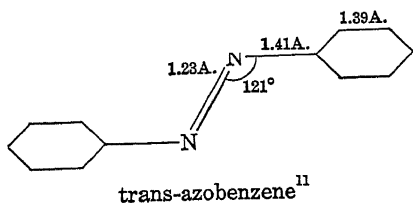
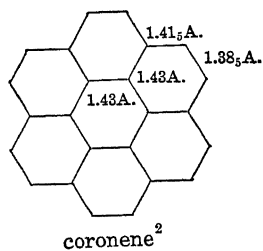
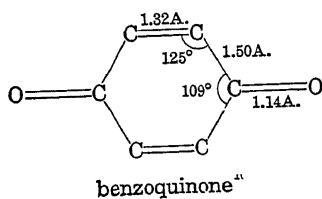
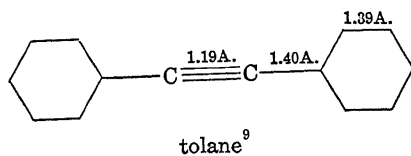
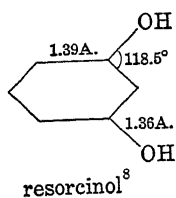
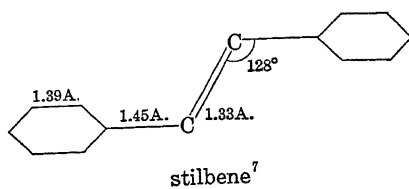
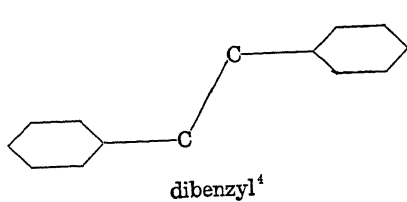
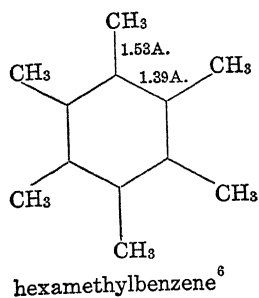
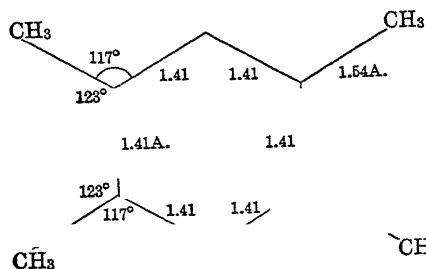


(32) **Covalent Bond Distances and Bond Angles:** Mainly in the last fifteen years a tremendous amount of data on covalent bond lengths and bond angles has been gathered by X-ray analysis of crystals. Perhaps the most intensive research has been carried out on carbon-carbon bond distances in organic compounds. The single bond, double bond and triple bond postulated by the organic chemist have been shown to have a physical basis and have characteristic bond distances of 1.54 Å, 1.33 Å, and 1.20 Å, respectively. In many molecules, however, bonds are not fixed as single or double bonds but are intermediate in length between 1.33 Å and 1.54 Å. This is in accordance with the theory of resonance between different valence bond structures described by Pauling.<sup>1</sup> A very simple treatment leads to the correlation of double bond

<sup>12</sup> D. Crowfoot, C. W. Bunn, B. W. Rogers-Low, and A. Turner-Jones, *The Chemistry of Penicillin*, chap. XI (Princeton, N. J.: Princeton University Press, 1949).

<sup>1</sup> *The Nature of the Chemical Bond* (Ithaca, N. Y.: Cornell University Press, 1938).

TABLE I



character with bond distance. Benzene has equal contributions from the Kekule structures (XII and XIII) and each bond may therefore be regarded as being 50 per cent a double bond and 50 per cent a single bond. The observed bond distance in benzene is 1.39 Å and therefore a curve can be drawn <sup>2</sup> (Fig. 57)

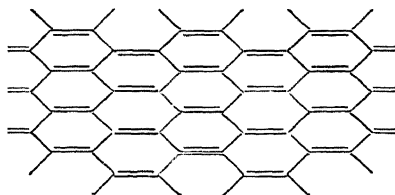


XII



XIII

with the ordinates representing bond distance and the abscissae double bond character, through the three points 1.33 Å (100 per cent) 1.39 Å (50 per cent) and 1.54 Å (zero double bond character). A fourth point is obtained from the graphite bond distance of 1.42 Å. In graphite resonance may be assumed between a large number of valence bond structures of the type shown, and each



bond has therefore  $\frac{1}{3}$  double bond character. This value, corresponding to 1.42 Å, fits the curve drawn through the other three points. The symmetry of the benzene molecule necessitates all six bonds being equal but this is not the case with condensed ring aromatic hydrocarbons where bonds in different parts of the molecules must be slightly different. Such variations have been observed in the coronene molecule <sup>3</sup> and in certain other polycyclic hydrocarbons. More refined quantum mechanical calculations of bond distances <sup>4</sup> are also in agreement with the experimental measurements. The dimensions of some organic molecules which contain carbon-carbon bonds are collected in Table I.

Some very interesting bond lengths have been found in compounds containing a chain of carbon atoms usually with alternating single and double bonds

<sup>2</sup> L. Pauling and L. O. Brockway, *J. Am. Chem. Soc.*, **59**, 1223 (1937).

<sup>3</sup> J. M. Robertson and J. G. White, *J. Chem. Soc.*, 607 (1945).

<sup>4</sup> C. A. Coulson, *Nature*, **154**, 797 (1944).

<sup>5</sup> J. M. Robertson, *Proc. Roy. Soc.*, **A142**, 659 (1933).

<sup>6</sup> L. O. Brockway and J. M. Robertson, *J. Chem. Soc.*, 1324 (1939).

<sup>7</sup> J. M. Robertson and I. Woodward, *Proc. Roy. Soc.*, **A162**, 568 (1937).

<sup>8</sup> J. M. Robertson, *ibid.*, **A157**, 79 (1936).

<sup>9</sup> J. M. Robertson and I. Woodward, *ibid.*, **A154**, 187 (1936); **162**, 568 (1937).

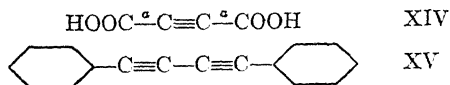
<sup>10</sup> J. M. Robertson, *ibid.*, **A150**, 106 (1935).

<sup>11</sup> J. J. DeLange, J. M. Robertson, and I. Woodward, *ibid.*, **A171**, 398 (1939).

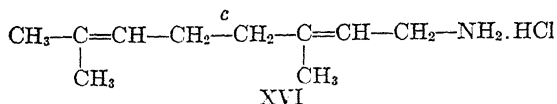
<sup>12</sup> R. B. Corey, *J. Am. Chem. Soc.*, **60**, 1598 (1938).

<sup>13</sup> G. Albrecht and R. B. Corey, *J. Am. Chem. Soc.*, **61**, 1087 (1939); J. D. Dunitz and J. M. Robertson, *J. Chem. Soc.*, 148 (1947).

or single and triple bonds. Certain formal single bonds show large contractions from the normal single bond distance of 1.54 Å. In acetylene dicarboxylic acid (XIV) the bonds *a* measure 1.43 Å. For diphenyl diacetylene <sup>14</sup> (XV) the



central bond of the chain is 1.39 Å. One of the most interesting contractions is found in geranylamine hydrochloride <sup>15</sup> (XVI) where the central carbon-carbon bond *c* is 1.44 Å. While it is possible to understand qualitatively that



there may be some contraction in these bond lengths the magnitude of the effect is surprisingly large.

It is not possible to describe here all bond distances measured involving other atoms as well as carbon, but two organic groups have been the subject

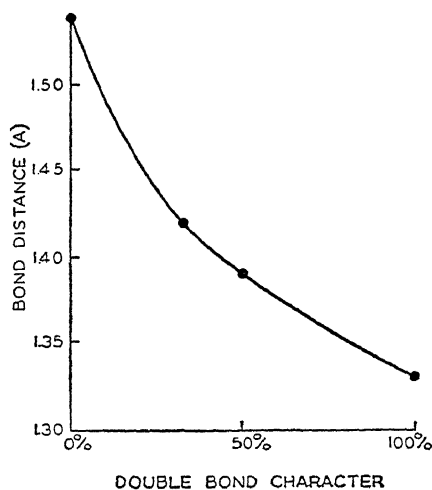


FIG. 57.

of much discussion. Both the carboxyl group  $-\text{COOH}$  and the nitro group  $\text{NO}_2$  should be symmetrical according to resonance theory, i.e., the two carbon oxygen distances and the two N—O distances should be equal. In oxalic acid dihydrate <sup>16</sup> a small difference is found between the C—O bonds but this difference is within the possible experimental error. The original structure determination of *p*-dinitrobenzene <sup>17</sup> gave large distortions in the molecule but, from a later analysis, Llewellyn <sup>18</sup> claimed that the nitro-group is symmetrical and coplanar with the benzene ring within the limits of experimental error. However, the published Fourier contour map in this later work does seem to show a distortion of the nitro-

group. In both cases the group probably is symmetrical in a free molecule but in the crystal the environment of the oxygen atoms is not the same. In

<sup>14</sup> E. H. Wiebenga, *Z. Krist.*, **102**, 193 (1940).

<sup>15</sup> G. A. Jeffrey, *Proc. Roy. Soc.*, **A183**, 388 (1945).

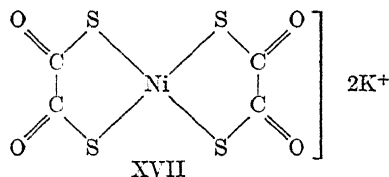
<sup>16</sup> J. M. Robertson and I. Woodward, *J. Chem. Soc.*, 1817 (1936).

<sup>17</sup> R. W. James, G. King, and H. Horrocks, *Proc. Roy. Soc.*, **A153**, 225 (1935).

<sup>18</sup> F. J. Llewellyn, *J. Chem. Soc.*, 884 (1947).

the hydrated carboxylic acids where crystal structure depends on hydrogen bonding there may well be small differences in the C—O distances. Similarly the high electronegativity of the nitro-group might make it subject to distortion in the crystal. However, more accurate and extensive experimental measurements are required for compounds of both types.

The bond angles of carbon can be predicted on theoretical grounds to be tetrahedral for single bonded carbon and coplanar and at  $120^\circ$  for aromatic compounds and these predictions are fully confirmed by the experimental measurements, except where distortions occur from steric effects. The angles given in Table I for durene seem slightly distorted because of the tendency of the adjacent methyl groups to move apart. The covalent bond angles of the transition metals have been very fully investigated because of the importance of the many complexes formed by these metals in both the classical and modern theories of stereochemistry. The two most important types of these structures are those in which the metal forms six octahedral bonds and the structures in which the metal directs four coplanar bonds to the corners of a square. The first may be exemplified by  $(\text{NH}_4)_2 \text{PtCl}_6$ . Hybridization of two of the  $d$  electronic orbitals with one  $s$  orbital and three  $p$  orbitals gives six equal Pt—Cl bonds directed to the corners of a regular octahedron. In the square coplanar type of coordination  $dsp^2$  hybridization gives four equal bonds at right angles as in potassium nickel dithio-oxalate (XVII).<sup>19</sup>



(33) **The Hydrogen Bond:** A hydrogen bond or bridge is formed between two electronegative atoms and is ionic in character. From X-ray analyses of crystals it is possible to measure the distance AB in the bond  $A \cdots H \cdots B$  and if this distance is significantly shorter than the normal van der Waals distance between A and B bonding is assumed. Hydrogen bonds have been detected in the systems  $\text{F} \cdots \text{H} \cdots \text{F}$ ,  $\text{O} \cdots \text{H} \cdots \text{O}$ ,  $\text{N} \cdots \text{H} \cdots \text{N}$ ,  $\text{N} \cdots \text{H} \cdots \text{F}$ ,  $\text{N} \cdots \text{H} \cdots \text{O}$ . For two oxygen atoms the criterion of hydrogen bonding is a distance of 2.5 to 2.9 Å between the oxygens. As an example of hydrogen bonding in an organic crystal we may consider the structure of oxalic acid dihydrate<sup>16</sup> (Fig. 58). Each water molecule has three hydrogen bonds directed from it to the oxygens of different carboxyl groups. Two of these are about equal at 2.87 Å and 2.84 Å while the third is 2.52 Å, the shortest hydrogen bond known between two oxygens. The two oxygen atoms of the carboxyl group are thus differentiated in a physical as well as in a crystallographic sense as one is attached to a water molecule by means of a short hydrogen bond and the other oxygen by a long

<sup>19</sup> E. G. Cox, W. Wardlaw, and K. C. Webster, *J. Chem. Soc.*, 1475 (1935).

hydrogen bond. Some writers have differentiated hydroxyl bonds, formed between two  $\text{—OH}$  groups from true hydrogen bonds. On this basis atom 2 which forms the weaker bond to water (Fig. 58) might be considered to be more of a hydroxyl oxygen than a keto oxygen. On the other hand Dunitz and Robertson<sup>12,20</sup> suggest that in oxalic acid and the similar acetylene dicarboxylic

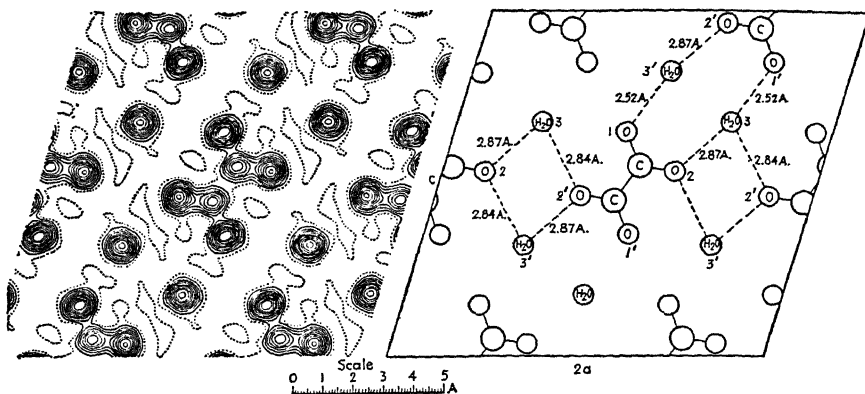


Fig. 58. Electron density contour map for oxalic acid dihydrate; projection along  $b$  axis, covering two unit cells. (Robertson and Woodward.)

acid dihydrate the transfer of the carboxylic hydrogen to water with the formation of an oxonium ion would leave a net negative charge on one oxygen of the carboxyl group which would give this oxygen atom the shorter bond. Brill, Hermann and Peters<sup>21</sup> in fact claim that atom 1 is the hydroxyl oxygen of the carboxyl group. Resonance of course will tend to equalize the two  $\text{C—O}$  bonds but it is suggested that resonance is incomplete and that one oxygen has more of the hydroxyl oxygen character than the other.

The crucial test of locating definitely an individual hydrogen atom in a structure largely composed of much heavier atoms cannot be carried out successfully by X-ray analysis. From the structures deduced from the X-ray data the hydrogen atom in a hydrogen bond between two oxygen atoms might be mid-way between the atoms, closer to one than the other or oscillating between the pair. It may eventually be possible to answer these important questions by means of diffraction of neutrons.

One further point arises from the structures of oxalic acid and related compounds. In the projection of Fig. 58 the hydrogen bond system of atoms 1-2-3-1'-2'-3'-1 appears to be a closed circuit. In actual fact it is an open spiral as the return from atom 3' to atom 1 reaches the molecule one translation along  $b$  from the molecule containing atom 2. This spiral arrangement is very important in organic structures and, in fact, where a hydrogen bond system is formed in an organic crystal it is the geometry of the hydrogen bonding

<sup>20</sup> *J. Chem. Soc.*, 142 (1947).

<sup>21</sup> *Naturwissenschaften*, 677 (1939).

which seems to determine the arrangement of molecules in the crystal. Resorcinol<sup>8</sup> (*m*-dihydroxybenzene) has the hydrogen bond system shown in projection in Fig. 59. The hydrogen bonds in this crystal measure 2.66 Å and 2.75 Å and, once again, the three dimensional arrangement is a spiral throughout the crystal. In pentaerythritol,<sup>22</sup>  $C(CH_2OH)_4$ , however the hydrogen bonds form a square of side 2.69 Å and the crystal consists of a series of sheets, molecules in one sheet being connected together by hydrogen bonds.

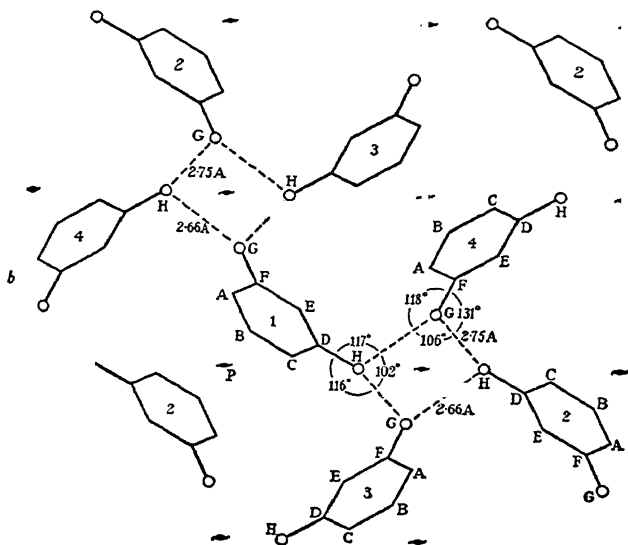


FIG. 59. The structure of resorcinol,  $C_6H_4(OH)_2$  (Robertson).

The structure of ice has been investigated by Barnes<sup>23</sup> who showed that each oxygen atom is tetrahedrally coordinated to four others. The hydrogen positions of course are not determined but Bernal and Fowler<sup>24</sup> suggested that polarization of each water molecule could give a tetrahedral distribution of positively and negatively charged parts of the molecule leading to the observed structure. Glycine,  $NH_2 \cdot CH_2 \cdot COOH$ , has hydrogen bonds measuring 2.76 Å and 2.88 Å and it is to be expected that hydrogen bonding is of the highest importance in the structures of all amino-acids and proteins. Other important crystals in which hydrogen bonding has been detected are urea,  $CO(NH_2)_2$  (2.98 Å, 3.03 Å), boric acid  $H_3BO_3$  (2.71 Å), sodium bicarbonate,  $NaHCO_3$  (2.55 Å) and potassium dihydrogen orthophosphate,  $KH_2PO_4$  (2.54 Å).

(34) **Anomalous Structures:** Rigid deductions concerning crystal and molecular symmetry made from space group theory may not be valid in all cases.

<sup>22</sup> F. J. Llewellyn, E. G. Cox, and T. H. Goodwin, *J. Chem. Soc.*, 883 (1937).

<sup>23</sup> *Proc. Roy. Soc.*, A125, 670 (1929).

<sup>24</sup> *J. Chem. Phys.*, 1, 515 (1933).



The symmetry given by the crystal as a whole may not be that of an individual unit cell with atoms fixed at definite points. Symmetry may be achieved statistically by a random arrangement of certain atoms and also by a time averaging process, i.e., rotation or oscillation of groups of atoms.

Defect structures are those in which crystallographically equivalent sites are not all occupied by the same kind of atom. Mixed crystals of KCl and KBr have the cation positions all filled with  $K^+$  ions but the  $Cl^-$  and  $Br^-$  ions are distributed at random among the anion positions. Crystals of perfectly definite composition may have such a random structure.  $Li_2Fe_2O_4$  has the sodium chloride structure but the  $Li^+$  and  $Fe^{3+}$  ions are distributed at random among the cation sites. This is possible because these two ions have approximately equal radii and the invariant composition is due to their difference in valence, for an excess of one over the other would leave the crystal as a whole electrically charged. Where the ions randomly distributed have the same valence, a continuous range of composition often results. A second type of defect structure is one in which the lattice is incomplete and the "holes" are distributed at random. Pyrrhotite,  $FeS$  consists of a rigid structure of sulfur atoms but the positions which should be occupied by iron atoms are not all filled and, on analysis, the substance is found always to contain an excess of sulfur over iron. It is known that many interstitial compounds vary in composition and here the smaller atoms do not all fill the equivalent positions assigned to them from space-group theory.

The simplest example of group rotation in a crystal is that of KCN. This has the sodium chloride structure and the potassium ions occupy the usual positions. The  $CN^-$  ion is therefore required to have the same symmetry as  $Cl^-$ , which is impossible for any fixed position of the atoms. The  $CN^-$  ion must be rotating in such a manner as to give it the required symmetry from the mean atomic positions over a period of time. In long chain groups or molecules it occasionally happens that rotation takes place about the long axis. Hendricks<sup>25</sup> has shown that this occurs for  $C_5H_{11}NH_3Cl$ . Space-group symmetry requires a tetragonal molecule which is quite impossible on any conventional ideas about the geometry of a hydrocarbon chain. The tetragonal symmetry is achieved by rotation about the long axis and when the crystals are taken to a very low temperature the structure changes. Another important example is that of monoclinic sulfur. Chemical evidence indicates that the molecule in this allotrope is the same as in the stable orthorhombic modification. However, the space-group is  $P2_1/a$  with six molecules in the unit cell<sup>26</sup> which requires that two of the molecules must have centers of symmetry. Either then, the molecule is not the puckered eight-membered ring assumed (Fig. 54) or an average symmetry center is attained by oscillation or rotation of the molecule. This point has still to be cleared up, but the second possibility appears more likely.

<sup>25</sup> *Nature*, 126, 167 (1930).

<sup>26</sup> J. T. Burwell, *Z. Krist.*, 97, 123 (1937).

All types of abnormal structures show up in the intensities of the X-ray reflections and, in cases where such structures have definitely been established, agreement has been obtained between the observed and calculated values of the X-ray intensities and this agreement could not occur with any other type of structure. In most cases the investigators have been driven to postulating the abnormal structures only after all normal structures proved to be impossible.

#### X-RAY DIFFRACTION BY PARTIALLY ORDERED MATERIALS

(35) **Small Particles:** Where a substance has no crystallinity at all the X-ray scattering is simply a diffuse background. Therefore, if the crystallites which make up a powder sample are extremely small the diffraction lines tend to broaden out. Above a crystal size of  $10^{-5}$  cm a very narrow, parallel beam of X-rays gives extremely sharp powder lines, whereas below this limit the lines gradually broaden and eventually become diffuse haloes for extremely small crystallites. In practice, slightly divergent X-ray beams are used and it is necessary to correct for the finite breadth of the line given by larger crystals. This is most simply done by recording the X-ray pattern of the substance under investigation mixed with a powder which is known to have a particle size greater than  $10^{-5}$ . Thus the broadening effect at any diffraction angle due to divergence of the beam can be calculated.

The first correlation of line breadth with particle size was made by Scherrer<sup>1</sup> who used the equation

$$\beta = B - b = 2 \sqrt{\frac{\ln 2}{\pi}} \frac{\lambda}{D} \sec \theta$$

$$0.94 \frac{\lambda}{D} \sec \theta \quad (35.1)$$

$\beta$  is the breadth of the line in radians, taken as the angular distance between two points at which the intensity has half the maximum value;  $B$  is the breadth observed and  $b$  the normal breadth of a line from crystallites larger than  $10^{-5}$  cm, recorded under the same experimental conditions.  $\lambda$  is the X-ray wavelength,  $D$  the diameter of the crystallites and  $\theta$  the Bragg angle. Seljakow,<sup>2</sup> and Bragg,<sup>3</sup> by different reasoning arrived at the corresponding relations

$$\beta_{\text{Seljakow}} = 0.92 \frac{\lambda}{D} \sec \theta \quad (35.2)$$

$$\text{and} \quad \beta_{\text{Bragg}} = 0.89 \frac{\lambda}{D} \sec \theta \quad (35.3)$$

The difference between these three equations is small but they apply only to

<sup>1</sup> *Göttinger Nachrichten* (1918).

<sup>2</sup> *Z. Physik*, 31, 439 (1925).

<sup>3</sup> *The Crystalline State* (London: George Bell & Sons, Ltd., 1933).

spherical particles and a more general relation was deduced by Laue.<sup>4</sup>

$$\eta = 0.0885 \left[ B' \cos \theta - \frac{1}{B'} \left( \pi \frac{r}{R} \right)^2 \cos^3 \theta \right] \quad (35.4)$$

Here  $\eta$  is a number which can be related to the shape and size of the crystal,  $r$  is the radius of the cylindrical specimen and  $R$  the radius of the camera.  $B'$  is the line breadth defined in this case as the area under the photometric trace across the line divided by the maximum intensity. In this treatment it is assumed that all the crystals of the powder are the same size, which is probably incorrect for most samples, and while attempts have been made to introduce distribution functions for particle size, the true distribution is in general unknown and the calculated mean size may not be the true mean size. It should be noted also that such calculations give the size of crystallites only and there is no information concerning the unit particle of the powder which may be an aggregate of crystallites.

Other causes of line broadening are variations in unit cell dimensions in different crystallites, thermal movement of the atoms and randomness in the crystal structure. The crystal size effect, however, may be distinguished by the proportionality of line broadening to  $\sec \theta$ , a relation which is not shown in line broadening due to other causes.

(36) **Glasses:** One of the most remarkable results of X-ray examination of the solid state has been the almost complete disappearance of "amorphous" materials. If we take amorphous to mean having a completely random structure, then such a material would give no interference maxima with X-ray diffraction and conversely, any material whether solid, colloidal or liquid which gives even diffuse diffraction arcs, corresponding to the sharp rings of good powder photographs must have some degree of order in its structure. The nature of the order is of course not clear without detailed examination. It may be a preferential system of packing atoms or molecules in relative motion which appears as an average over a period of time, as is the case with most liquids, or it may be that the atoms are at rest and that there is a fairly constant distance between each atom and its nearest neighbor but that larger interatomic distances do not have the same regularity as would be the case in a true crystal. Glasses fall into this category of partially ordered materials as X-ray photographs show in general two or more diffuse haloes.

The general mathematical theory relating structure to diffraction ring intensities in such cases is applicable both to liquids and to glasses. The most general expression for the scattering of X-rays by matter is that which is applicable where the molecule is so large that the unit particle of the substance is one molecule and all diffraction effects are due to interatomic distances within the molecule. The intensity formula was developed first by Debye<sup>1</sup>

<sup>4</sup> *Z. Krist.*, **64**, 115 (1926).

<sup>1</sup> *Ann. Physik*, **46**, 809 (1915).

for a structure containing two kinds of atoms,  $p$  and  $q$ :

$$I = \frac{I_0 e^4}{m^2 c^2 R^2} \left( \frac{1 + \cos^2 2\theta}{2} \right) \sum_p \sum_q f_p f_q \frac{\sin S r_{pq}}{S r_{pq}} \quad (36.1)$$

$I_0$  is the intensity of the incident beam,  $2\theta$  the scattering angle and  $R$  the distance from specimen to film or other detecting device;  $(1 + \cos^2 2\theta)/2$  is the polarization factor ( $P$ ) as in crystal diffraction,  $f_p$  and  $f_q$  are the scattering powers of the atoms  $p$  and  $q$  which are a distance  $r_{pq}$  apart and  $S = 4\pi \sin \theta/\lambda$ . We can write Equation (36.1)

$$I \propto P \sum_p \sum_q f_p f_q \frac{\sin S r_{pq}}{S r_{pq}}$$

and if only one kind of atom is present

$$I \propto P_n f^2 \sum \frac{\sin S r_n}{S r_n} \quad (36.2)$$

A maximum in functions (36.1) or (36.2) means that there is a preferred interatomic distance in the structure given by the value of  $r$  for this maximum and corresponding to the observed diffraction halo at the appropriate value of  $\sin \theta/\lambda$ . If interatomic distances are known, these can be inserted directly in Equations (36.1) and (36.2) but if they are unknown it is necessary to introduce a distribution function  $g(r)$  giving the average distribution of scattering matter round any atom. Thus the number of atoms between spheres of radius  $r$  and  $r + dr$  round an atom is  $4\pi r^2 g(r) dr$ . Hence from (36.2)

$$I \propto P_n f^2 \sum_n \frac{\sin S r_n}{S r_n} g(r) dr \quad (36.3)$$

or<sup>2</sup>

$$I = k P_n f^2 \left\{ 1 + \int_0^\infty 4\pi r^2 [g(r) - \rho] \frac{\sin S r_n}{r_n} dr \right\} \quad (36.4)$$

and writing

$$\frac{I/kP - f^2}{f^2} = \varphi(s)$$

$$s\varphi(s) = \int_0^\infty 4\pi r [g(r) - \rho] \sin S r dr$$

By applying Fourier's integral theorem it can be shown that

$$4\pi r^2 g(r) = 4\pi r^2 \rho + \frac{2r}{\pi} \int_0^\infty S \varphi(S) \sin r S dS \quad (36.5)$$

In the application of Equation (36.3) the method is one of trial and error, various forms of the function  $g(r)$  being evaluated and tested against the observed

<sup>2</sup> F. Zernike and J. A. Prins, *Z. Physik*, 41, 184 (1927).

data. Equation (36.5), however, makes it possible to deduce  $g(r)$  directly from the observed intensities, but, as it stands, this equation is only applicable to substances containing one kind of atom, e.g., monatomic liquids. However, it has been found possible to generalize this equation and Warren, Krutter and Morningstar<sup>3</sup> have used the relation

$$\Sigma K_m 4\pi r^2 \rho_m = \Sigma K_m 4\pi r^2 \rho_0 + \frac{2r}{\pi} \int_0^\infty S i(S) \sin r S dS \quad (36.6)$$

where  $\Sigma$  indicates summation over the molecular composition;  $r$  = distance from any atom;  $K_m$  = effective number of electrons per atom;  $4\pi r^2 \rho_m dr$  is the number of atoms, each multiplied by the effective number of electrons, between  $r$  and  $r + dr$  from the atom  $m$ ;  $\rho_0$  is the average number of electrons per unit volume;  $S = (4\pi \sin \theta)/\lambda$ ;  $i(S) = (I_{\text{e.u.m.}} - \Sigma f_m^2)/f_e^2$ ;  $I_{\text{e.u.m.}}$  = experimental intensity of unmodified scattering in electron units per molecule;  $f_m$  = atomic scattering factor and  $f_e = \Sigma f_m / \Sigma Z_m$ .

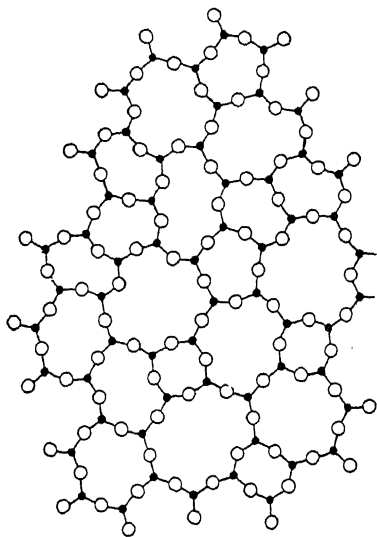


FIG. 60. Random structure of  $\text{SiO}_4$  tetrahedra (shown as triangles) in glass (Zachariasen).

A simple example of a structure worked out by the above methods is that of vitreous silica. This glass gives two diffraction haloes which have spacings rather close to, but not identical with those of cristobalite the high temperature crystalline modification of silica. The two most probable explanations of the vitreous state were (a) that silica glass consists of very small crystallites of cristobalite, the broadening of the diffraction maxima being due to the very small number of planes reflecting in each crystallite, and (b) that there is an extended network of  $\text{SiO}_4$  tetrahedra which is distorted in such a way as to destroy most of the crystalline character. Particle size calculations from the width of the diffraction bands showed that, on the crystallite theory, the hypothetical

particles had the dimensions of only one unit cell and so could hardly be called crystalline. In addition, the softening of glass on heating could not be explained from this theory as even a microcrystalline aggregate might be expected to have a sharp melting point. A much more probable explanation is the extended network suggested by Zachariasen<sup>4</sup> (Fig. 60). The  $\text{SiO}_4$  tetrahedra are shown as triangles and all the Si—O covalent bond are normal. The

<sup>3</sup> *J. Am. Ceram. Soc.*, **19**, 202 (1936).

<sup>4</sup> *J. Am. Chem. Soc.*, **54**, 3841 (1932).

randomness occurs in the method of linking tetrahedra to form the whole structure. This picture of glass is one of a liquid which has been cooled so quickly from the molten state that there has not been time to build up a regular crystal structure. The strong covalent Si—O bonds give the substance its high viscosity and prevent spontaneous transformation into a crystalline form. Since a different amount of energy is required to break down each mesh the continuous softening range is easily explained.

On the basis of this model, Warren<sup>5</sup> calculated the maxima required by Equation (36.3) assuming that the atoms surrounding a given silicon atom are at regular distances from this atom up to a radius of 5.2 Å and beyond this range the distribution of scattering matter is continuous. The results are in very good agreement with the actual intensity distribution observed. A direct calculation from Equation (36.5) gave the first peak (Si—O) at 1.62 Å compared with 1.60 Å found for this bond in the crystalline silicates. The other peaks were in accordance with the idea that each silicon atom is surrounded tetrahedrally by oxygen and two such tetrahedra are joined so that the Si—O—Si system is approximately collinear. Around this region the tetrahedra are oriented at random. Similar types of structure have been confirmed for many substances in the vitreous state.

The conditions for the formation of glasses, which are comparatively rare, have been investigated by Zachariasen.<sup>6</sup> The energy of the structure is of obvious importance as a large difference between the energy of the glass structure and that of the corresponding crystal structure would cause a rapid transition from one to the other, and it is believed that this condition is not often fulfilled. For an oxide glass of composition  $A_mO_n$  to be formed Zachariasen deduced that

- (1) No oxygen atom can be bound to more than two A atoms.
- (2) The coordination of oxygen round A must be low.
- (3) The oxygen polyhedra must share only corners.
- (4) At least three corners of the oxygen polyhedra must be shared.

Under these conditions the only oxides which should occur in the vitreous state are  $B_2O_3$ ,  $SiO_2$ ,  $GeO_2$ ,  $P_2O_5$ ,  $As_2O_5$ ,  $P_2O_3$ ,  $As_2O_3$ ,  $Sb_2O_3$ ,  $V_2O_5$ ,  $Sb_2O_5$ ,  $Cb_2O_5$  and  $Ta_2O_5$ .

(37) **Fiber Structures:** Both natural and synthetic fibers consist of very long chain molecules the long axes of which are at least approximately parallel. If there is no regularity of orientation in other directions then the only structural information which can be obtained by X-ray diffraction is in connection with periodicities along the chain axes. In most fibers, however, this is not quite the case. There is local three dimensional crystallinity covering a comparatively small number of unit cells in directions perpendicular to the long molecular axis. For example, stretched plastic sulfur may be regarded as a bundle of very small crystallites each of which shows three-dimensional crystal-

<sup>5</sup> *Phys. Rev.*, **45**, 657 (1934).

<sup>6</sup> *Loc. cit.*, ref. 4.

linity, but the different crystallites have a common orientation in one direction only, that of the fiber axis. In other directions they are packed together at random. This is important in considering the meaning of X-ray fiber photographs. A simple rotation photograph about the fiber axis gives, in favorable cases, something similar to a single crystal photograph, showing discrete spots arranged in layer lines. The reflections are not usually nearly as sharp as those from a single crystal as the tendency of the constituent crystallites to be not quite parallel may smear the reflections out over a fairly large area.

The two most serious limitations to analysis of X-ray fiber diagrams are the difficulty of indexing reflections and incompleteness of the observed data. It can readily be understood that the greater diffuseness of reflections in fiber work increases the possibility of reflections overlapping, which is serious enough with single crystals. For single crystals, however, it is possible when such difficulties arise to use oscillation or moving film techniques in order to index the reflections unambiguously. The random orientation of crystallites in the directions perpendicular to the fiber axis prevents the use of these methods for fibers and in large unit cells there are always uncertainties in assigning indices. In a fiber, also, there are generally submicroscopic regions where the structure is amorphous and, hence, the background scattering is much heavier than for single crystals, with consequent loss of data concerning weak reflections.

In very few cases can it be said that fiber structures have been established with the certainty of many crystal structures, but a large amount of interesting information has been obtained. In one respect fiber structures have a certain advantage over crystals. It is known that the molecular direction along the polymer chain almost certainly coincides with the fiber axis itself and therefore the periodicity along this axis has a direct application to distances along the molecular chain. The unit cell dimension corresponding to this periodicity in a fiber is a submultiple of the molecular length, i.e., the molecule repeats within itself. In plastic sulfur this is a true periodicity, but for some protein fibers it is merely an approximate intra-molecular periodicity, that of the basic polypeptide chain.

One further question which concerns fiber structures in general is whether any intermolecular reflections occur, i.e., reflections due to regularity of the chain lengths as well as regularity within the chains. In synthetic polymers such as the polyoxymethylenes such small angle reflections may be observed, but in naturally occurring fibers the evidence is conflicting;  $\alpha$ -rubber shows no small angle scattering<sup>1</sup> but in the  $\beta$ -rubber modification a spacing has been found which corresponds to 24 times the simple repeat unit.<sup>2</sup> It is not clear, however, that this represents the actual chain length and not simply a larger repeat unit within the chain.

Plastic sulfur is formed when molten sulfur in the viscous state is chilled suddenly. The allotrope is then rubber like and seems to be amorphous, but when stretched into long fibers it gives an X-ray diffraction pattern which

<sup>1</sup> R. W. G. Wyckoff and R. B. Corey, *J. Biol. Chem.*, **114**, 407 (1936).

<sup>2</sup> G. W. Pankow, *Helv. Chim. Acta*, **19**, 221 (1936).

shows a high degree of orientation. Meyer and Go<sup>3</sup> have examined this pattern and have deduced the chain configuration shown in Fig. 61. The periodicity along the fiber axis is 9.26 Å which fits the proposed model exactly if the normal sulfur bond distances and bond angles are assumed. There are 112 atoms in the unit cell which therefore contains parts of 14 chains of this type. The physical properties of sulfur are in accordance with the transformation from the eight-membered rings of rhombic sulfur to the long chains of the

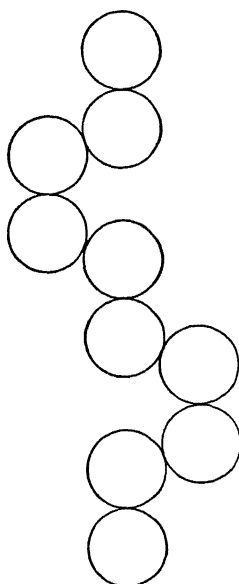
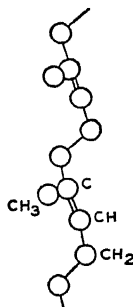
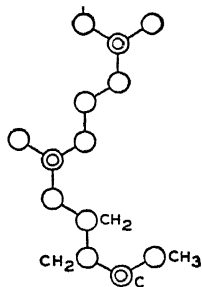


Fig. 61.

9.26 Å

 $\beta$ -GUTTA-PERCHA

RUBBER HYDROCHLORIDE

Fig. 62.

plastic form. While the picture is not yet quite clear, particularly as regards liquid sulfur just above the melting point, it appears that the rings break on melting, or at a slightly higher temperature. With further increase in temperature the short chains so formed join together and, in the viscous state of molten sulfur, these chains are tangled with each other at random. A sudden cooling then gives this type of structure in the solid state and orientation of the chains takes place on stretching the material.

Natural rubber has been extensively investigated by X-rays. In the normal state there is no evidence of regular orientation but, when the sample is stretched beyond 80 per cent, a characteristic diffraction pattern appears. The reflections do not change position on further stretching but increase in intensity.<sup>4</sup> Rubber and its isomers consist of polymerized isoprene chains ( $-\text{CH}_2-\text{C}(\text{CH}_3)=\text{CH}-\text{CH}_2-$ )<sub>n</sub> and two of the configurations which this

<sup>3</sup> *Helv. chim. Acta*, 17, 1081 (1934).

<sup>4</sup> Hauser and Mark, *Kolloidchem. Beihefte*, 22, 63 (1926).



type of chain can adopt are shown in Fig. 62 which gives the skeletons of  $\beta$ -gutta percha and rubber hydrochloride ( $-\text{CH}_2-\text{CCl}(\text{CH}_2)=\text{CH}-\text{CH}_2$ )<sub>n</sub>. Both these substances have been the subject of detailed investigations by Bunn<sup>5,6</sup> and while, for the reasons explained above, fiber analysis can never have the accuracy of single crystal analysis the general configuration is established in these two cases with some certainty.

The structure of native cellulose has been postulated from a combination of chemical evidence and X-ray diffraction patterns. The repeat unit for cellulose,<sup>7</sup> (a) is shown in Fig. 63 with the related units for chitin<sup>8</sup> (b) and chitosan

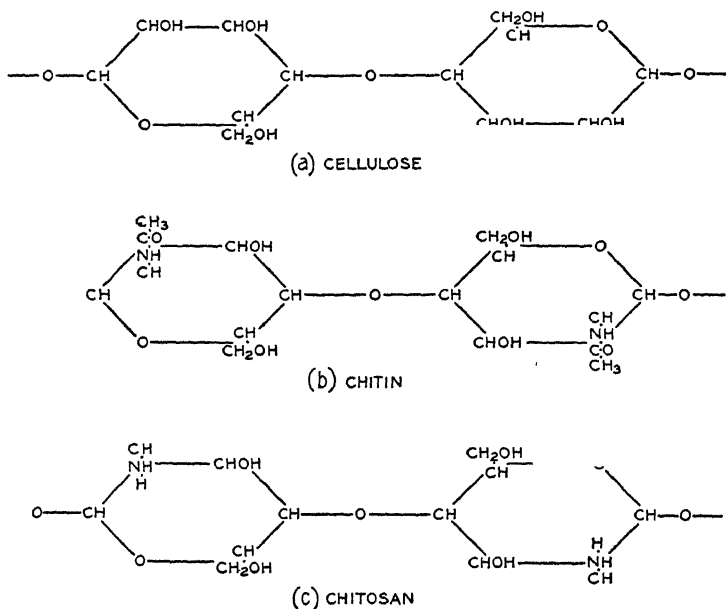


FIG. 63.

(c). Alternate chains in the cellulose unit cell have the  $\beta$ -glucose residues pointing in opposite directions and for chitin and chitosan the arrangement is similar.

The most ambitious of all X-ray investigations is the attempt to solve the structure of the proteins. In fibrous protein structures the most important contributions to present day ideas on the subject have come from Astbury and coworkers.<sup>9,10</sup> The chemical evidence from the break-down of proteins suggests

<sup>5</sup> K. H. Meyer and H. Mark, *Ber.*, **61**, 1939 (1928).

<sup>6</sup> C. W. Bunn, *Proc. Roy. Soc.*, **A180**, 40, 67, 82 (1942).

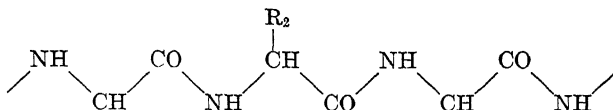
<sup>7</sup> Meyer and Misch, *Helv. Chim. Acta*, **20**, 222 (1937).

<sup>8</sup> Clark and Smith, *J. Phys. Chem.*, **40**, 863 (1936).

<sup>9</sup> *Nature*, **137**, 803 (1936).

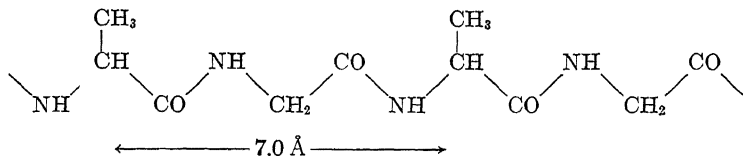
<sup>10</sup> *Trans. Faraday Soc.*, **34**, 378 (1937).

that these very large molecules are formed from polypeptide chains (XVIII) and that the great diversity of proteins is due to the great variety of side-chains  $R_1$ ,  $R_2$ ,  $R_3$ , etc. Now fibroin, the polypeptide of silk, is believed to consist

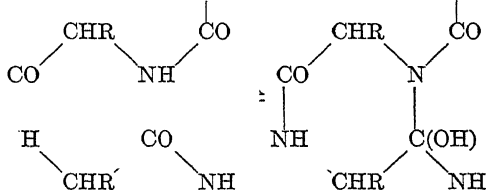


XVIII

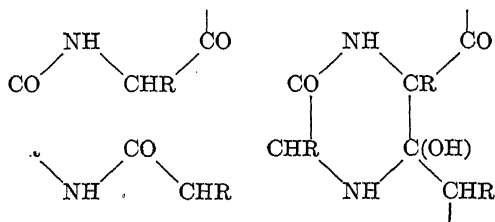
mainly of alternate glycine and alanine residues, giving a periodicity of  $7.0 \text{ \AA}$  calculated from normal bond distances and angles which is in excellent agreement with the observed spacing. The protein keratin in hair shows no simi-



larity to fibroin in its X-ray diffraction pattern in the normal state ( $\alpha$ -keratin) but does give a similar pattern when stretched ( $\beta$ -keratin). There is no true periodicity along the fiber axis but an approximate periodicity of  $3.5 \text{ \AA}$ . This is strong evidence that the only essential difference between the fibroin and  $\beta$ -keratin structures is in the side chains. The  $\alpha$ -keratin structure must be some sort of folded arrangement of the polypeptide chains and Astbury suggested a hexagonal type of folding giving closed rings by lactam-lactim interchange (XIX) or keto-enol interchange (XX). This arrangement would give a



XIX



XX

fiber periodicity in the unstretched state of about 5 Å in agreement with the observed value.

In stretched keratin there is a lateral spacing of 4.65 Å observed which may correspond to the distance between two polypeptide chains held together by interaction between the =NH and =CO groups of different chains. If this is correct then the  $\beta$ -keratin structure type consists of a two dimensional polypeptide grid with the side chains sticking out at right angles to this grid (Fig. 64). Folding to the  $\alpha$ -keratin form is assumed to take place by buckling the

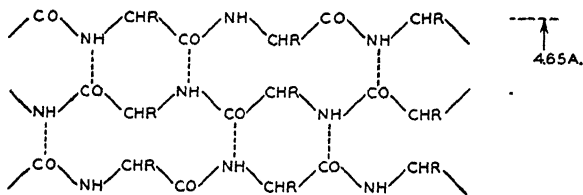


FIG. 64.

folds out of the grid plane and, as would be expected, the 3.5 Å and 4.65 Å spacings are destroyed on folding. The stretching of keratin involves breaking intramolecular linkages. Prolonged steaming in the stretched state allows the formation of new linkages and, after this process, the  $\beta$ -form is stable. If, however, the linkages are broken and the fiber is immediately allowed to contract in steam it is found that it becomes actually shorter than the original  $\alpha$ -form. This suggests a new type of folding of polypeptide chains to give a "supercontracted" state.

This observation is important in connection with the structure of the protein myosin which is the principal component of muscle. The myosin chains in a relaxed muscle seem to correspond to the  $\alpha$ -keratin folded form. From this state they can be stretched to a  $\beta$ -form or contracted to a supercontracted form. The comparative insensitivity of keratin as compared with myosin is explained by the fact that keratin has a much higher sulfur content due to the larger proportion of the amino acid cystine. The —S—S— cross-linkages in keratin are disrupted on stretching from the  $\alpha$ - to the  $\beta$ -form and it is only after this that supercontraction occurs. In myosin however there are very few S—S cross linkages so that supercontraction is more easily achieved.

Only one type of protein gives X-ray diffraction patterns which cannot be correlated with one state or another of the keratin-myosin group. This is the group containing collagen and gelatin and all members within the group have pronounced similarities. One suggestion is that in collagen the polypeptide chains are partly of a *cis* form and partly of a *trans* form instead of being all *trans* as in the  $\beta$ -keratin type. Astbury's suggested structures for the four main types of fibrous protein are shown in Fig. 65 where (a) is the  $\alpha$ -keratin type, (b) the  $\beta$ -keratin type, (c) the collagen type and (d) the supercontracted type.

It is important to stress just what has been achieved in this work. The most important features are (1) the recognition of polypeptide chains as the

basis of protein structure combined with the hypothesis of the submolecular pseudo-repeat unit; (2) observations of similar types of structure in different proteins and their correlation with physical properties, and (3) the establishing of the importance of cross-linkages in protein structures, particularly the —S—S— cross-linkage. Undoubtedly, the polypeptide chains are folded in the  $\beta$  and supercontracted forms and the suggested methods of folding are in accordance with the observed data. On the other hand it is not clear that other types of folding are incompatible with the observations and we may expect this question to be one of the most important aspects of future protein research.

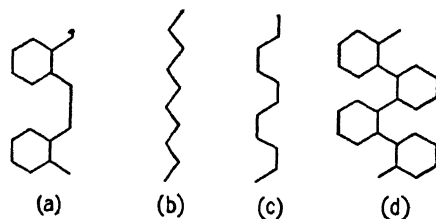


FIG. 65.

(38) **Crystalline Proteins:** It has been suggested, and with some justification, that the distinction between crystalline or globular proteins on the one hand and the fibrous proteins on the other is artificial. Denaturation of globular proteins seems to result in the formation of ordinary polypeptide chains of the  $\beta$ -keratin form and it appears that the globular proteins are composed of multi-folded chains. The folded keratin structures may be regarded as being intermediate between the  $\beta$ -form of the fibrous proteins and the globular proteins. However, from the point of view of X-ray analysis there is a very real practical difference between the two groups. With crystalline proteins a vastly greater amount of X-ray data is obtainable and here also a very high degree of internal regularity is shown both from the sharpness of the X-ray reflections and the small spacing planes from which reflections can be observed. While it does not appear to be possible to carry out a complete structure analysis for one of these complex substances in the sense that simpler molecules have been analyzed, many of the techniques of ordinary structure analysis, notable Patterson syntheses, have been applied to crystalline proteins, and valuable information has been obtained about the shapes and sizes of the molecules in a much more direct manner than is the case for fibrous proteins. On the experimental side it is possible to use oscillation as well as rotation photographs, and in fact there seems to be no fundamental reason for not using moving-film methods although, because of practical difficulties, this does not seem to have been done so far. With very large protein unit cells a new experimental technique has been used by Crowfoot and Schmidt.<sup>1</sup> In such crystals any crystal orientation will have several sets of planes in a position to reflect and, consequently, it is possible to use a stationary crystal with monochromatic X-radiation, thus shortening exposure times considerably. Detailed single crystal X-ray work has been carried out on the proteins insulin, lactoglobulin, the tobacco mosaic virus and horse methemoglobin. All these crystals have

<sup>1</sup> *Nature*, 155, 504 (1945).

been photographed in both the wet and the dry states and the results are in agreement with Svedberg's figure of 35,000 or a multiple of this number for protein molecular weights. A molecule in the solid state may be regarded as a number of atoms connected by chemical bonds of one type or another and not bound to atoms outside the group by anything stronger than van der Waals forces, and it is therefore not possible to determine molecular weights by X-ray analysis without finding every atomic position. If Svedberg's measurements are assumed correct it is found that the rhombohedral insulin unit cell contains one molecule, the horse methemoglobin cell two molecules and both the orthorhombic and tabular forms of lactoglobulin eight molecules. Further confirmation of the Svedberg molecular weight for insulin is obtained by comparison of the corresponding Patterson projections on the basal plane (0001) for the wet and air dried crystal.<sup>2</sup> Both projections have a group of 18 peaks round the origin which change position as a whole on changing from the wet to the air-dried crystal. It seems therefore that these peaks correspond to interatomic vectors within one molecule and, on this basis, one unit cell contains one molecule. From these Patterson diagrams Wrinch<sup>3</sup> put forward the cyclol theory of protein structure. An insulin molecule is depicted as a single polyhedron formed in such a way that side chains project from one surface but leave the other surface with no side chains. According to this theory, all globular protein molecules have one surface which is essentially the same. This view has been strongly criticized. Bernal<sup>4</sup> has stressed the fact that the peaks in the (0001) Patterson projection for insulin lie on a hexagonal network and he associated this with close packing both of the molecules in the crystal and of sub-units within one molecule. Some very detailed single crystal photographs have been obtained from the tobacco mosaic virus<sup>5</sup> which has a molecular weight of 1,850,000. It is suggested that the molecules may be approximately spherical and of radius 80 to 100 Å.

The most far-reaching X-ray work on crystalline proteins has been that on horse methemoglobin.<sup>6</sup> The molecular weight is 66,700 and in the wet crystals just over half the unit cell volume is occupied by solvent. The method of phase determination by step-wise reversible swelling of the crystals by water has already been discussed (Section 26) and, in addition, a modification of the isomorphous replacement method was used by allowing heavy metal salt solutions of known concentration to take the place of water. One-dimensional Fourier projections and two-dimensional Patterson projections were computed for varying degrees of hydration. The intramolecular reflections (from small-spacing planes) were very little affected by the introduction of the heavy ions but the intensities of some low angle reflections were drastically altered. This

<sup>2</sup> *Chem. Rev.*, **28**, 215 (1941).

<sup>3</sup> *Proc. Roy. Soc.*, **A160**, 59 (1937).

<sup>4</sup> *Proc. Roy. Soc.*, **A170**, 75 (1939).

<sup>5</sup> Crowfoot and Schmidt, *loc. cit.*, ref. 1.

<sup>6</sup> Boyes-Watson, Davidson, and Perutz, *Proc. Roy. Soc.*, **A191**, 83 (1947) Perutz, *ibid.*, **A195**, 474 (1948).

indicates that the solvent does not change the molecular configuration, but rather enters in between adjacent molecules and the cell dimensions are changed by shearing of one layer of molecules over another as well as by expansion of the intermolecular distances. The preliminary picture of the crystal structure given by these workers is shown in Fig. 66. The molecules are approximately cylindrical with diameter 57 Å and height 34 Å. The space group symmetry requires that each molecule consists of two identical halves although a difference of a very few atoms between the two halves would have no effect on the X-ray

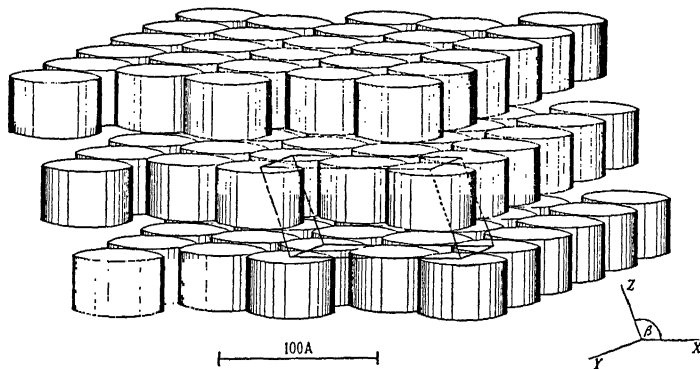


FIG. 66. Packing of methemoglobin molecules in the crystal structure, showing layers of close-packed molecules separated by liquid. One unit cell is shown in the foreground on the right. (Boyes, Watson, Davidson and Perutz.)

observations. The one-dimensional Fourier projection shows four very distinct peaks corresponding to four layers of scattering matter parallel to the base of the cylinder. The next stage in the investigation was the computation of a three-dimensional Patterson synthesis, using all the available X-ray data and evaluated in 31 sections throughout the unit cell. In such a complex structure, of course, the assignment of individual interatomic vectors is impossible, but if there is a certain internal regularity within the molecule, such as would be given by the parallel polypeptide chains, then certain vectors will repeat many times throughout the molecule and build up recognizable peaks in the Patterson maps. This appears, indeed, to be the case, for while the main peaks found are small compared to the general background, they certainly appear to be significant, and can be interpreted in broad outline in terms of folded polypeptide chains. The approximate picture of the internal structure of the molecule which was suggested was an arrangement of polypeptide chains parallel to the base of the cylinder. The chains have a fold at short range giving an outstanding vector at 5 Å parallel to the chain lengths. There is also folding at rather longer range which may be due to folding of the chains backwards and forwards upon themselves at an average distance between successive folded parts of the chain of about 10.5 Å, or alternatively to closed loops of polypeptide chains. The whole

assembly is arranged in four layers parallel to the base of the cylinder at an average distance of 9 Å.

### THE SIGNIFICANCE OF X-RAY ANALYSIS

(39) **Uniqueness of the Solution:** We have indicated that most crystal structure analyses are carried out by essentially indirect methods and it has been assumed that only one set of atomic positions will give the observed diffraction pattern. Since the intensities of the X-ray reflections depend on the interatomic vectors, any two structures which have equivalent sets of vector distances will give rise to the same intensities. It is well known that two structures which can be made to coincide by a translation, a reflection, a rotation or a combination of these operations give the same diffraction pattern and such structures are termed congruent. The important question which arises is whether non-congruent structures can have the same vector distances and hence give the same diffraction pattern.

The first case of this kind was discovered by Pauling and Shappell<sup>1</sup> who found that a special position in the space group  $Ia\bar{3}$  gives two non-congruent structures for the  $+x$  and  $-x$  values of the  $x$ -parameter, which have the same vector distances. This ambiguity also occurs in the space-group  $Ia\bar{3}d$ .

The possibility of such ambiguities has been examined in some detail by Patterson<sup>2</sup> for the one-dimensional case. A one-dimensional periodic function

may be represented by placing points at varying intervals around the circumference of a circle and two such non-congruent arrangements which have the same vector distances are shown in Fig. 67. Patterson describes two structures related in this way as a homometric pair. A large part of this work consisted of an examination of cyclotomic sets, i.e., groups of structures in which the points are

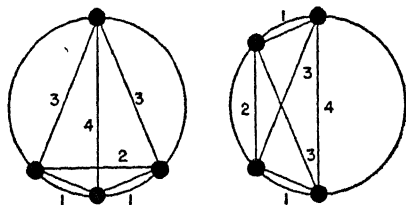


FIG. 67. A simple homometric pair. The distances are the same but the points are in different arrangements. (Patterson).

placed on the circumference of a circle at  $r$  of the  $n$  vertices of an inscribed regular polyhedron. An examination of 2664 cyclotomic sets resulted in the discovery of 390 homometric pairs, 7 homometric triplets and 3 sets of quadruplets for the cyclotomic sets  $r = 8$ ,  $n = 16$ . In this diagram the full lines connect points forming an invariant sub-set while variable points are connected by dotted lines. Most of the distance lines have been omitted in order to simplify the picture. Two interesting results are that if two cyclotomic sets (consisting of the  $n - r$  positions unoccupied in the original sets) are also homometric, and a cyclotomic set where  $r = n/z$  is either congruent with or homometric with the complementary set. These observations reduce the labor

<sup>1</sup> *Z. Krist.*, 75, 128 (1930).

<sup>2</sup> *Phys. Rev.*, 65, 195 (1944).

in searching for all homometric groups. It is also shown that there are counterparts in two and three dimensions to the homometric pairs found in one dimension.

At first sight these ambiguities are rather disturbing, as they seem to destroy the basic assumption of X-ray analysis, which is that only one structure will give calculated diffraction effects in quantitative agreement with the observed diffraction pattern. However, it must be remembered that these ambiguities have been deduced on purely mathematical grounds and if they occurred in

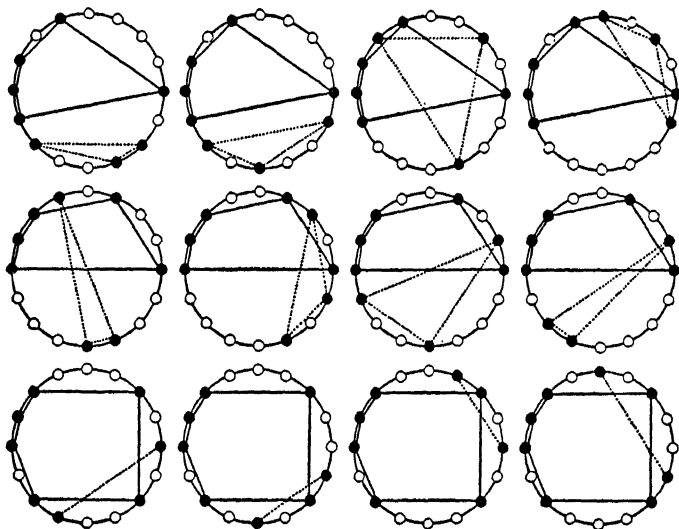


FIG. 68. Three homometric quadruplets from the cyclotomic sets:  $N = 16$ ,  $r = 8$  (full circles). Most of the distance lines are omitted for clarity. An invariant subset for each quadruplet is outlined in full lines. Variant points are connected by dotted lines. Examination of the open circles will show that the first two and the last two of each quadruplet form complementary pairs. (Patterson.)

crystal structure work they would probably take the form of alternative structures ridiculous in terms of chemistry. Nevertheless, X-ray analysis should be confirmed as far as possible by other physical measurements. The possibility of two structures equally in agreement with X-ray data, packing considerations, chemical theory, optical measurements and crystal morphology appears to be extremely remote.

The most probable source of a serious mistake in structure analysis is the interchange in position of two atoms of approximately equal scattering power. For example, if an oxygen atom in the structure is exchanged for a nitrogen atom, the calculated X-ray diffraction pattern will be almost unchanged and only the utmost precision in the techniques employed can distinguish the two cases. Fortunately this type of ambiguity is usually recognized as a danger at



the start of an investigation and all possibilities are examined. The situation is more serious in complicated overlapping projections where different combinations of atoms might give rise to the same type of composite peak in a Fourier map, and three-dimensional analysis may be necessary to clarify the structure.

There is also the possibility that an essentially incorrect structure may give a sufficient measure of agreement to be accepted. Here the only safe procedure is to accept a structure as correct only when there is quantitative agreement between the calculated and observed values of the structure factors for such a large number of reflections that the possibilities of error are negligible, or, if the Fourier method of refinement is used, the contour maps should be so clear that there is no doubt about the atomic positions. In this connection it is worth noting that the presence of a heavy atom, the position of which is accurately known, gives fictitiously good agreement between calculated and observed intensities as the greater part of most structure amplitudes is due to this single atom.

These remarks apply with even greater force to partial structure analyses where a structure model is deduced from a few reflections either because complete data are unobtainable or because the problem itself is so complex that a complete and rigorous solution cannot be found. It does not follow that such incomplete analyses are not worth-while, for important contributions to structural chemistry have been made in this way, particularly where other physical evidence supports the proposed structure. However, it should be realized that such solutions are only consistent with the X-ray data and not established by it. Similarly, the deduction of molecular shapes from cell dimensions alone may be very misleading. Bunn<sup>3</sup> has strikingly illustrated how molecules of very different shapes can fit into the same unit cell.

(40) **Accuracy of Crystal Coordination Determined by X-ray Analysis:** In a simple structure where all or nearly all the atoms are in special positions, the accuracy of atomic coordinates and interatomic distances may be as high as the accuracy with which the cell constants have been measured. In more complex structures, however, where the Fourier series method of refinement is usually employed, the question of the accuracy of the method is of obvious importance in view of the frequent correlation of bond-type with bond distance. Four possible sources of error are important:

(1) *Finite summation errors.* For a strictly accurate representation of electron density distribution an infinite Fourier series is required. In practice, the series is terminated at the limit of observation set by the wavelength of the X-rays used, most frequently  $\text{CuK}\alpha$ . This termination of the series introduces errors dependent on the convergence of the series which in turn depends on the atoms present and their thermal movement.

(2) *Errors in the observed coefficients of the series.* These include errors in the actual intensity estimations and extinction and absorption effects.

<sup>3</sup> *Chemical Crystallography* (New York: Oxford University Press, 1945), p. 187.

(3) *Computational inaccuracies.* These may arise because it is not practicable to use standard mathematical tables and "rounding-off" errors may occur by use of two-figure<sup>1</sup> or three-figure<sup>2</sup> sine and cosine strips.

(4) *Errors in drawing projection maps.* These depend on the scale and graphical methods used. Accuracy may be lost where the summation totals are simply interpolated linearly as compared with the method of fixing contour positions by drawing graphs of all the rows and columns of the summation table.

The first two of these sources of error have been investigated by Booth.<sup>3-6</sup> A comparison of  $F$  values obtained for the same structure by different workers using quite independent methods of measurement showed that the experimental errors lay on a normal error curve and the probable error for any reflection could be calculated. From this it was possible to calculate the displacements of atomic centers in organic structures due to these inaccuracies. Booth showed that these errors are fairly small, 0.008 Å for a two-dimensional series and 0.003 Å for a three-dimensional series. The effect of finite summation errors is rather greater but it was only possible to make a rigorous calculation in the diatomic case. However, one important result was deduced, viz., that finite summation errors, generally assumed to be the most important of all, are of the same order of magnitude in both two and three-dimensional Fourier series.

A more empirical approach has been made to the problem by Robertson and White.<sup>7</sup> A two-dimensional Fourier projection was studied for a hypothetical structure containing twelve atoms in general positions, which had separations between 1.0 Å and 1.4 Å. The structure factors were calculated up to the limit of  $\text{CuK}_\alpha$  radiation using an average hydrocarbon scattering curve so that the results are applicable to a wide range of organic compounds. By computation of several Fourier series the effect on atomic positions of finite summation errors and both random and systematic errors in the structure factors were examined. The conclusions are that the maximum error in bond-distance estimations should not be greater than 0.03 Å and the probable error is about 0.015 Å for a range of structure factors to  $\sin \theta = 1$ , for  $\text{CuK}_\alpha$  radiation provided that photometric or very careful visual estimates of intensities of reflections are made and the crystals used are small and symmetrical in cross-section. These errors may well be exceeded if unsuitable crystal specimens are used or if the Fourier series is terminated at a lower value of  $\sin \theta$ . It was found that an average value of several crystallographically independent bond distances is extremely reliable, the error being less than  $\pm 0.01$  Å. These figures

<sup>1</sup> C. A. Beevers and H. Lipson, *Proc. Phys. Soc.*, **48**, 772 (1936).

<sup>2</sup> J. M. Robertson, *Phil. Mag.*, **21**, 176 (1936).

<sup>3</sup> *Trans. Faraday Soc.*, **42**, 444 (1946).

<sup>4</sup> *Proc. Roy. Soc.*, **A188**, 77 (1947).

<sup>5</sup> *Ibid.*, **A190**, 482 (1947).

<sup>6</sup> *Ibid.*, **A190**, 490 (1947).

<sup>7</sup> *Ibid.*, **A190**, 329 (1947).

do not, of course, necessarily represent the ultimate accuracy obtainable by Fourier series or other methods. The most obvious experimental refinement is the extension of the observed reflections by the use of shorter wavelength X-rays in order to reduce the finite summation errors. As yet this has been done in comparatively few cases. The presence of heavy atoms in the structure will reduce the accuracy of the coordinates of the lighter atoms both because of the slower convergence of the series due to the smaller temperature effect of the heavy atoms and also because of the greater effect of experimental inaccuracies in this case on the atomic coordinates of the lighter atoms.

Acknowledgment is made as indicated for permission to reproduce certain figures in this chapter. Figs. 18, 19, 43, 56, 59, 66, The Royal Society (Proceedings); Figs. 37, 41, 58, The Chemical Society (Journal); Figs. 39, 40, American Physical Society (*J. Chem. Phys.*); Figs. 42, 67, 68, Physical Review; Fig. 60, Am. Chem. Soc. (Journal); Fig. 48, Cambridge University Press (Crystal Chemistry—Evans).

## CHAPTER V

### THE COLLOIDAL STATE AND SURFACE CHEMISTRY

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### COLLOIDAL SOLUTIONS

#### INTRODUCTION <sup>1</sup>

About the beginning of the modern period in chemistry, as the science began a rapid development along descriptive and analytical lines and the concept of solubility became well defined, investigators observed that substances ordinarily considered insoluble (gold, arsenic trisulfide, sulfur, aluminum hydroxide, etc.) could sometimes exist in apparently homogeneous solutions. On account of the instability of these solutions, the indirect manner in which they often had to be prepared, and a special deportment in certain other respects, it gradually became customary to distinguish between these "pseudo-solutions," as Selmi (1847) called them, and ordinary solutions of sugar, common salt, alcohol, and the like. The pioneering work of Richter, Berzelius, Wöhler, Frankenheim, Schneider, Wackenröder, Baudrimont, Selmi, Kuhn, Faraday, Crum, Pean de

\* Deceased September 7, 1943.

<sup>1</sup> General references: Alexander, *Colloid Chemistry, Theoretical and Applied*, Vol. I, *Theory and Methods* (New York: Chemical Catalog Co., 1926); Vol. II, *Biology and Medicine* (New York: Chemical Catalog Co., 1928); Vol. III, *Technological Applications* (New York: Chemical Catalog Co., 1931); Vol. IV, *Technological Applications* (New York: Chemical Catalog Co., 1932); Vol. V, *Theory and Methods: Biology and Medicine* (New York: Reinhold Publishing Co., 1944); Vol. VI, *General Principles and Specific Industries, Synthetic Polymers and Plastics* (New York: Reinhold Publishing Co., 1946). Bancroft, *Applied Colloid Chemistry* (2d ed.; New York: McGraw-Hill Book Co., Inc., 1926); Dean, *Modern Colloids* (New York: D. Van Nostrand Co., Inc., 1948); Freundlich, *Kapillarchemie* (4th ed.; Vol. I., Leipzig: Akad. Verlag, 1930); Vol. II, 1932, the most comprehensive monograph on the subject; Rideal, *An Introduction to Surface Chemistry*, 2d ed.; (London: Cambridge University Press, 1931); Svedberg, *Colloid Chemistry*, (2d ed.; New York: Chem. Catalog Co., 1928); Hartman, *Colloid Chemistry*, 2d ed. (Boston: Houghton Mifflin Co., 1947); Hauser, *Colloidal Phenomena* (New York: McGraw-Hill Book Co., Inc., 1939); Thomas, *Colloid Chemistry* (New York: McGraw-Hill Book Co., Inc., 1934); Weiser, *Colloid Chemistry*, 2d ed. (New York: John Wiley & Sons, Inc., 1949); Lewis, Squires and Broughton, *Industrial Chemistry of Colloidal and Amorphous Materials* (New York: The Macmillan Co., 1942); Alexander and Johnson, *Colloid Science* (London: Oxford Univ. Press, 1949); Kruyt, *Colloid Science*, Vol. II (New York: Elsevier Pub. Co., 1949); McBain, *Colloid Science* (Boston: Heath & Co., 1950).

Saint Gilles, and others<sup>2</sup> in preparing and describing the "pseudo-solutions" was given a certain unity by the classification and lasting nomenclature proposed by Thomas Graham.<sup>3</sup>

By means of a new technique, the separation of dissolved substances by differential diffusion through membranes, which he called "dialysis," Graham distinguished between the inorganic pseudo-solutions mentioned above as well as solutions of proteins, gums, tannin, polysaccharides and the like, on the one hand, and ordinary solutions containing small molecules of known composition, on the other hand. The dissolved materials of the former class, displaying a very low rate of diffusion and leaving apparently amorphous solids upon evaporation of the solvent, were called "colloids" (glue-like) in contrast with the other class of substances, the "crystalloids." Solutions of colloids were designated as "sols," or specifically as "hydrosols," "alcosols," "ethersols," etc., depending upon the medium; and the gelatinous amorphous solids obtainable from sols were referred to as "gels," or specifically, as "hydrogels," "alcogels," etc. The process of dispersing a gel or colloidal solid to form a sol was called "peptization." The spontaneous shrinkage of a gel with the separation of a free liquid phase was termed "syneresis." Although Graham recognized that certain substances could form either colloidal or crystalloidal solutions, he often disregarded these and spoke as if the classification of substances into colloids and crystalloids were mutually exclusive.

During the five decades following Graham's work, the ever increasing number of experimental and theoretical investigations of colloidal solutions provided a richness of data that encouraged efforts toward systematizing them into a new branch of science. At this stage appeared the first books of a general nature and the first special periodical, *Zeitschrift für Chemie und Industrie der Kolloide*, later *Kolloid-Zeitschrift*, which began in 1907. It gradually became clear that the feature common to colloidal solutions and responsible for their characteristic behavior is a state of subdivision intermediate in coarseness between that of the ordinary or crystalloidal solutions and gross homogeneous bodies of pure substances; the emphasis shifted from "colloidal substances" to a "colloidal state of aggregation," as universal as the gaseous, liquid, or solid states.<sup>4</sup>

<sup>2</sup> Summaries of early work in the field of colloids may be found in the following references, which include the monographs of a general nature published before 1910: Hatschek, *The Foundations of Colloid Chemistry* (New York: The Macmillan Co., 1925 [a selection of classical papers]); Svedberg, *Die Methoden zur Herstellung kolloider Lösungen anorganischer Stoffe* (Dresden: Steinkopf, 1909 [contains references to most of the experimental work antedating 1908]); Von Weimarn, *Die Allgemeinheit des Kolloidzustandes* (2d ed.; Dresden: Steinkopf, 1925), Vol. I; Guareschi, "Colloid Contributions of Selmi," *Kolloid-Z.*, 8, 113 (1911); Bancroft, "Baudrimont as Colloid Chemist," *J. Phys. Chem.*, 28, 256 (1924); Bredig, *Anorganische Fermente* (Leipzig: Engelmann, 1901); Lottermoser, *Ueber anorganische Kolloide* (Stuttgart: Ahrens Sammlungen, 1901); Zsigmondy, *Zur Erkenntnis der Kolloide* (Jena: Fischer, 1905); Müller, *Allgemeine Chemie der Kolloide* (Leipzig: Barth, 1907); Freundlich, *Kapillarchemie* (Leipzig: Akad. Verlag, 1909); W. Ostwald, *Grundriss der Kolloidchemie* (Leipzig: Steinkopf, 1909); *Kolloid-Z.*, Vol. I (1907), contains a collection of abstracts of papers published after 1850.

<sup>3</sup> *Phil. Trans. Roy. Soc., London*, 151, 183 (1861); *J. Chem. Soc.*, 17, 318 (1864).

<sup>4</sup> The new point of view was experimentally developed by von Weimarn (1905-1908) and

(1) **Dispersed Systems:** Both ordinary and colloidal solutions are now recognized to be in a broad sense *dispersed systems* that comprise a *dispersion medium* and a *dispersed phase*,<sup>1</sup> and to differ principally in degree of heterogeneity. In the typical ordinary solution, the dispersed part or solute is subdivided into units, often single small molecules or ions, that are of the same order of magnitude as atomic dimensions and the range of molecular forces, that is, a few Ångströms.<sup>2</sup> Whenever one or more dimensions of the dispersed units appreciably exceed this magnitude, regardless of whether the unit is one or more molecules, behavior characteristic of colloidal solutions may be expected to appear in some form or another. In some cases, as in the gold sols, it has

TABLE I  
NUMBER AND TOTAL SURFACE OF PARTICLES AS A 1-CM CUBE  
IS SUBDIVIDED INTO SMALLER CUBES

Number of particles	Length of edge in cm	Total surface in cm <sup>2</sup>
1	1	6
10 <sup>3</sup>	10 <sup>-1</sup>	6 × 10
10 <sup>6</sup>	10 <sup>-2</sup>	6 × 10 <sup>2</sup>
10 <sup>9</sup>	10 <sup>-3</sup>	6 × 10 <sup>3</sup>
10 <sup>12</sup>	10 <sup>-4</sup> (= 1 μ)	6 × 10 <sup>4</sup>
10 <sup>15</sup>	10 <sup>-5</sup>	6 × 10 <sup>5</sup>
		Limit of resolving power of microscope
		Well-defined Tyndall effect
10 <sup>18</sup>	10 <sup>-6</sup>	6 × 10 <sup>6</sup>
		Typical colloidal solutions
		Hemoglobin molecule
10 <sup>21</sup>	10 <sup>-7</sup> (= 1 mμ)	6 × 10 <sup>7</sup>
		Faraday gold sol
10 <sup>24</sup>	10 <sup>-8</sup> (= 1 Å)	6 × 10 <sup>8</sup>
		Atomic dimensions

been possible by X-ray analysis to demonstrate that the dispersed unit is a very small crystal fragment identical in structure with ordinary gold in bulk, even when its size is no greater than 10 to 20 Å.<sup>3</sup> At the surface of such a particle there must be a relatively abrupt transition in properties from those peculiar to bulk crystalline gold on the one side to those characteristic of the surrounding medium in bulk on the other side. When the particle is so exceedingly small, it is obvious that a relatively large fraction of the gold atoms in the particle are in or closely adjacent to the surface. Inasmuch as it is now generally believed that atomic and molecular forces are not effective over distances much exceeding atomic dimensions, it has become customary to generalize from the case of gold and similar sols and to consider that a dispersed unit over a few Å in diameter, whether a single molecule or not, constitutes a distinct phase

summarized in his *Grundzüge der Dispersoidchemie* (Dresden: Steinkopf, 1911). It was also explicitly stated by W. Ostwald, *Kolloid-Z.*, 1, 291, 331 (1907), and *Grundriss der Kolloidchemie*, 1909.

<sup>1</sup> Terminology introduced by W. Ostwald, *loc. cit.*

<sup>2</sup> The Ångström, i.e., 10<sup>-8</sup> cm, will be subsequently represented by the symbol Å.

<sup>3</sup> Scherrer, in *Zsigmondy, Kolloidchemie* (3d ed., Leipzig: Spamer, 1920), p. 387 ff.

with an interfacial region where it comes in contact with its environment.<sup>4</sup> In the range of dimensions represented by typical colloidal solutions, this interfacial region becomes enormous compared with that of the same amount of material in bulk (Table I), and any phenomenon associated with the surface may become very pronounced even though it is imperceptible under ordinary conditions.

Ostwald's classification of dispersed systems, exclusive of ordinary solutions in which the "solute" cannot be identified as a solid, liquid, or gas, according to the state of aggregation of the phases involved is given in Table II. As

TABLE II  
CLASSIFICATION OF DISPERSED SYSTEMS

Dispersion medium	Dispersed phase	Dispersed system
1. Gas	Gas	(Capable of only a transient existence)
2. Gas	Liquid	Mists
3. Gas	Solid <sup>1</sup>	Smokes; solid foams
4. Liquid	Gas	Foams and gas emulsions
5. Liquid	Liquid	Emulsions; sols and gels
6. Liquid	Solid <sup>1</sup>	Suspensions; sols and gels
7. Solid <sup>1</sup>	Gas	Solid foams
8. Solid <sup>1</sup>	Liquid	Solid emulsions
9. Solid	Solid	Gold ruby glass; alloys

<sup>1</sup> When one phase is solid, both phases may be continuous and intertangled as in a sponge so that no distinction can be made between the dispersion medium and the dispersed phase.

this classification indicates, colloidal solutions represent but two types of dispersed systems in general. However, the behavior in large part of all eight types of dispersed systems is found to be controlled by the same fundamental factors: *heterogeneity* and *interface effects* resulting therefrom. As a consequence, modern colloid science has expanded beyond the limits of colloidal solutions into a science of finely divided matter, i.e., "dispersoidology" (according to von Weimarn) or "capillary chemistry" (according to Freundlich), selecting, classifying, coordinating, and interpreting those phenomena that become evident when matter is highly subdivided and interfaces are much extended. Inasmuch as colloidal sols and gels (types 5 and 6 of dispersed systems) have received by far the most extensive investigation and the discussion of all types would have to be exceedingly superficial in a work of this scope, it will suffice to restrict the discussion largely to colloidal sols and gels as typical of dispersed systems. Other types will be dealt with only to the extent that they have contributed significantly to the understanding of the behavior of colloidal systems.

<sup>4</sup> An opposite point of view is defended by Buchner, in Alexander, *Colloid Chemistry* (1926), Vol. I, chap. 4, and by Procter, *Trans. Faraday Soc.*, 16, 40 (1921).

(2) **Classification of Colloids:** Numerous methods of classifying colloids have been proposed. One of the oldest is that of Wo. Ostwald who proposed *suspensoids* and *emulsoids*. The former includes suspensions of very fine particles of solids and, surprising to state, liquids. The particle size depends upon the method of preparation; maximum concentration for reasonable stability is usually rather small; stability is usually dependent, at least in aqueous systems on electrical charge; the stability is normally sensitive to electrolytes; flocculation by electrolytes and other agencies is usually irreversible. Emulsoids include colloidal solutions of jelly-forming systems, proteins, starch, etc., for which sensitivity to electrolytes is often nil or much less than the above group; concentrations may be quite high; flocculation or coagulation is often reversible and dissolution may occur spontaneously. The usual classification is into *lyophobic* (or *hydrophobic*) and *lyophilic* (or *hydrophilic*) systems, a method proposed by J. Perrin, 1905.<sup>1</sup> The “-phobic” and “-philic” refer to the absence or presence of attractive forces between dispersed phase and medium. The two classes correspond with the suspensoid-emulsoid classification. Freundlich proposed the terms “electrocratic” and “non-electrocratic,” the former referring to the colloidal solutions that are sensitive to electrolytes. In all events, it should be emphasized there are many transition cases that are difficult to classify.

The classification which we shall prefer is based upon the thermodynamic stability of the colloidal system. Many materials when “dissolved” or brought into contact with suitable liquids spontaneously pass into a dispersed form, and, as far as can be ascertained, form liquid systems that meet the various criteria of thermodynamic stability that can be applied. For various reasons they are naturally colloids, and the solutions formed are as stable as solutions of non-colloids. We call them “intrinsic colloids.” This class includes the two groups called by Staudinger “micellar colloids” and “molecular colloids,” and they are lyophilic colloids although the reverse is not true. The other colloids, the non-intrinsic group, represent in general dispersions of ordinary insoluble materials obtained by indirect methods, such as grinding or otherwise subdividing gross material, or precipitating the material under such conditions that the normal formation of a gross precipitate is prevented by special techniques, yielding essentially unstable suspensions which, by processes of recrystallization or solution and redeposition, will eventually break down the colloid state by formation of the more stable gross precipitate. This group may be also called the “extrinsic colloids,” meaning “accidental colloids.”

The largest group of “intrinsic colloids” includes the organic macromolecular substances, many of which occur in nature including proteins, cellulose, and related structural polysaccharides, starches, and related reserve polysaccharides, gums, hemicelluloses, bacterial polysaccharides, rubber, gutta percha, etc., various oxidized unsaturated oils, lignin, pectin, chitin, etc. In addition, during relatively recent times, many chemical derivatives of these natural products

<sup>1</sup> *J. chim. Phys.*, 3, 84 (1905).



have been made and many entirely new and synthetic macromolecular materials have been prepared, so that a new chemistry, the chemistry of macromolecules, has developed.

In order to emphasize the two features largely controlling colloidal behavior—small dimensions and the special properties of interfaces—the discussion of colloidal solutions will be developed from two points of view:

- (a) The Molecular Kinetic Behavior of Dispersed Systems, and
- (b) The Micellar Behavior of Dispersed Systems, or the Physical Chemistry of Interfaces.

Thus, in making use of such a classification the attempt is made to describe these systems in terms of (a) those properties of the colloidal solutions which are like those of the ordinary true solutions, and (b) those properties which are unique to the micellar systems.

#### MOLECULAR KINETIC BEHAVIOR OF COLLOIDAL SOLUTIONS

On the basis of the molecular kinetic theory the kinetic energy of suspended particles in a sol should be the same as the kinetic energy of a molecule. The, mean translational energy of a particle should be  $\frac{3}{2}kT$ , where  $k$  is the Boltzmann constant and  $T$  is the absolute temperature, and colloidal solutions should give osmotic pressure and show diffusion just as do ordinary solutions. A colloidal solution closely resembles the model from which the classical kinetic theory of ordinary solutions has been developed; the colloidal particles suspended in a fluid are equivalent to the solute molecules of an ordinary solution. In fact, the laws of so-called true solutions are to a considerable extent the laws of colloidal solutions. Furthermore, the agreement between fact and theory is often closer for colloidal than for ordinary molecular solutions. In connection with the comparison of experimental facts with the kinetic theory, colloidal systems possess two important advantages: first, the possibility of perceiving the kinetic unit in them with the ultramicroscope permits a much more detailed and searching test of theoretical deductions; and second, their kinetic behavior may be studied in concentrations (expressed in terms of the *number of kinetic units*) far lower, and therefore nearer the "ideal" of infinite dilution, than in the case of ordinary solutions of small molecules.

(3) **Brownian Movement:** The first significant step in the development of a molecular kinetic structure was made by the English botanist Brown<sup>1</sup> when he took particular notice of the continuous irregular vibratory motion, now called "Brownian motion," that is shown by pollen grains and other microscopic objects suspended in a liquid. He convinced himself that the motion was not due to capillary forces, evaporation, or mutual attraction or repulsion of the particles. The phenomenon was then generally neglected until the latter half of the century when the development of the kinetic theory of gases reawakened

<sup>1</sup> *Phil. Mag.*, 4, 161 (1828); 6, 161 (1829); 8, 41 (1830).

some interest. By the gradual elimination of such external factors as light, vibrations, electrical effects, convection currents, etc., as possible causes of the motion,<sup>2</sup> it became generally accepted that the oscillations of the small particles directly reveal the molecular movement of the surrounding liquid as pictured in the kinetic theory. It was suggested that the summated impacts of the

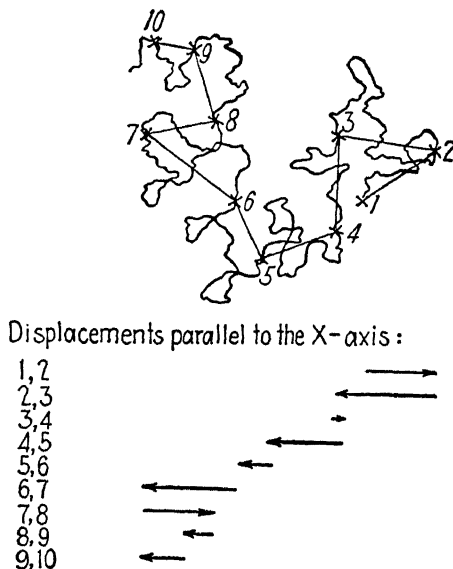


FIG. 1. Brownian-Motion Displacements. The continuous line represents the projection of the approximate path of a particle onto a fixed plane. The points locate the successive positions of the particle at uniform time intervals. The projections on the  $X$ -axis of the straight lines joining the successive points measure the separate displacements, indicated by  $\Delta_x$  or simply  $\Delta$ . The straight lines themselves represent the displacements parallel to the  $XY$ -plane, i.e.,  $\Delta_{xy}$ . The segments joining the actual spatial locations of the particle are symbolized as  $\Delta_{xyz}$ .

$$\overline{\Delta^2_{xy}} = 2\overline{\Delta^2_x} = 2\overline{\Delta^2_y} = 2\overline{\Delta^2_z};$$

and

$$\overline{\Delta^2_{xyz}} = 3\overline{\Delta^2_x}; \quad \text{and} \quad \overline{\Delta^2_x} = \frac{3}{8}\pi\overline{\Delta^2_x}.$$

These relations express the fact that the displacements have no preferred directions. In each case the bar over the symbol indicates the average of a large number of values. In the figure the displacements are obviously too few to give equality between the average positive and average negative displacements.

liquid molecules on all sides of a very small particle do not at every instant cancel exactly. Efforts naturally were then made to measure the speed of the moving particles in order to compare their kinetic energy with that of the liquid molecules at the same temperature.<sup>3</sup> Only later did it become evident that

<sup>2</sup> See, for instance, Wiener, *Ann. Physik*, (2) 118, 79 (1863); Gouy, *J. phys.*, 7, 561 (1888).

<sup>3</sup> Exner, *Ann. Physik*, 2, 843 (1900).

the path of a suspended particle is too irregular and zigzag to permit the determination of its velocity. It has been calculated that a colloid particle changes its direction over  $10^{20}$  times in a second.<sup>4</sup>

With the invention of the slit ultramicroscope, which revealed the very much more striking motion of ultramicroscopic particles, and with the application of the kinetic theory to dispersed systems by Einstein<sup>5</sup> and von Smoluchowski,<sup>6</sup> progress became rapid. The experimental investigations in the laboratories of Svedberg and of Perrin kept pace with the theoretical developments.

In the following paragraphs a number of the theoretical deductions in the form of equations are summarized, their concordance with experiment indicated, and their application to the determination of particle size briefly described. The classical equations are in part limited to spherical particles or molecules. For nonspherical particles the theory is more complicated, but it has become of significance in connection with the interpretation of data of diffusion, sedimentation velocity, viscosity, double refraction of flow, etc., in systems of certain high polymers and non-spherical protein molecules; the equations developed will be presented later (p. 540).

The Brownian motion may be quantitatively characterized (a) by measuring a large number of displacements of a single particle occurring in uniform time intervals parallel to a fixed line regardless of the actual path followed (Fig. 1) or (b) by noting the varying number of colloidal particles within a certain small volume of solution, again at regular time intervals, i.e., the spontaneous concentration fluctuations.

(4) **Distribution of Linear Displacement:** For displacements in the  $x$ -direction during a short time interval  $t$ , a given molecule or particle will have moved a distance  $\Delta_1$ , another  $\Delta_2$ , etc. Displacements will be both positive and negative. Although this is not at all a necessary restriction, we shall now assume that all the molecules are displaced by the average value  $\Delta$ . The mean diffusion of the particles through unit cross-section, along the  $x$ -axis of the cylinder shown in Fig. 2 will now be calculated.

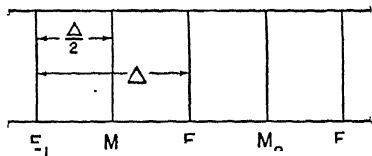


FIG. 2. Brownian Motion and Diffusion.  $\Delta$  is the root-mean-square displacement of the colloidal particles in time  $t$ .

For dilute solutions the mean displacement  $\Delta$  will be the same in various parts of the solution, even though the concentrations vary, because for all practical purposes the Brownian motion is due to bombardment by the solvent molecules. In the time interval  $t$  there will pass from left to right through plane  $E$  only those molecules which are less than  $\Delta$  distant to the left of  $E$ .

<sup>4</sup> Fowler, *Statistical Mechanics* (London: Cambridge University Press, 1929), p. 328.

<sup>5</sup> *Ann. Physik*, 17, 549 (1905); 19, 289, 371 (1906); Ostwald's *Klassiker*, No. 199.

<sup>6</sup> *Ann. Physik*, 21, 756 (1906); Ostwald's *Klassiker*, No. 207; *Physik. Z.*, 17, 557, 585 (1916).

But since only half of these molecules have positive displacements only half will pass through plane  $E$ . The amount of solute which passes through a  $1 \text{ cm}^2$  cross-section of plane  $E$  from left to right is  $\frac{1}{2}n_1\Delta$  where  $n_1$  is the concentration at the plane  $M_1$  in gram moles per cubic centimeter. Similarly the amount passing through from the right is  $\frac{1}{2}n_2\Delta$ . The net quantity of solute which diffuses across the plane from left to right in time  $t$  is  $\frac{1}{2}\Delta(n_1 - n_2)$ . Since  $\Delta$  is small,

$$n_2 - n_1 = \frac{dn}{dx} \Delta \quad (4.1)$$

so that the amount of solute which diffuses across the plane from left to right in 1 sec is given by

$$\text{Amount diffusing} = - \frac{\Delta^2}{2t} \frac{dn}{dx} \quad (4.2)$$

Since the diffusion constant,  $D$ , is defined as the amount which would diffuse through 1 cm in 1 sec under a unit concentration gradient, we may write as the general law of the particle

$$D = \frac{\Delta^2}{2t} \quad (4.3)$$

When the  $\Delta$ 's are not all equal,  $\Delta^2$  should be written as  $\bar{\Delta}^2$ , the average of the squares of the displacements.

The relationship between the diffusion constant  $D$  and the molecule or particle frictional coefficient  $f$ , i.e., the force required to give the particle unit velocity, was also derived by Einstein to give

$$D = \frac{RT}{Nf} \quad (4.4)$$

where  $N$  is the Avogadro number and  $R$  is the molar gas constant. When the suspended units are spherical and have radius  $r$ , then  $f = 6\pi\eta r$ , by Stokes's law, and hence

$$D = \frac{RT}{6\pi\eta r N} \quad (4.5)$$

Combinations of the Equations (4.3) and (4.5) gives

$$\bar{\Delta}^2 = \frac{RTt}{3\pi\eta r N} \quad (4.6)$$

so that it is possible to determine the Avogadro number by a study of the Brownian displacements of spherical particles.

The variation in  $\Delta$  from the mean is described by the normal probability function, i.e.,

$$P(\Delta_i) = \frac{1}{\sqrt{2\pi\bar{\Delta}^2}} e^{-\Delta_i^2/2\bar{\Delta}^2} \quad (4.7)$$

where  $P(\Delta_i)$  measures the relative frequency for the occurrence of the displacement  $\Delta_i$ .

Numerous observations have been compared with these equations in one form or another. The earlier work<sup>1</sup> partially confirmed Equation (4.6) by showing the relative effect of one or two variables upon  $\bar{\Delta}^2$ , the others remaining unknown. Complete tests of the equation were made by Perrin<sup>2</sup> and his co-workers, and by others, using relatively large particles of mastic or gamboge ( $r = 210$  to  $520 \text{ m}\mu$ ). Values of  $N$  calculated from the experimental values of the other variables fell between  $5.6$  and  $9.4 \times 10^{23}$ ;  $6.9 \times 10^{23}$  was considered the most trustworthy value, whereas the present accepted one is  $6.023 \times 10^{23}$ .

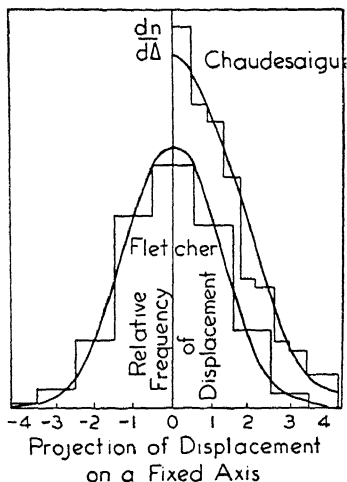


FIG. 3. Distribution of Brownian-Motion Displacements. The smooth curves are theoretical, the irregular curves are experimental. The sign of the displacements was disregarded by Chaudesaigues.

With more refined methods, involving semi-automatic or automatic photographic recording of the Brownian motion, Svedberg<sup>3</sup> obtained values for  $N$  of  $6.2$  and  $5.9 \times 10^{23}$  with aqueous dispersions of gold ( $r = 22 \text{ m}\mu$ ) and of mercury ( $r = 120$  to  $266 \text{ m}\mu$ ), respectively.

A painstaking investigation of the Brownian motion of oil drops suspended in a gas was made by Fletcher<sup>4</sup> in Millikan's laboratory under particularly favorable conditions: wall effects were absent, the frictional resistance exerted by the gas on the moving drop was accurately ascertainable, and a statistically adequate number of observations could be made upon a single particle.

For dispersions in a gas the usual form of Stokes's law is invalid. To correct it, the displacement equation must be multiplied by  $(1 + 0.86l/r)$  where  $l$  is the mean free path in the gas. From about 19,000 displacements of twelve oil drops, a mean value for  $N$  of  $(6.03 \pm 0.12) \times 10^{23}$  was obtained, in excellent agreement with the accepted value.

<sup>1</sup> Svedberg, *Z. Elektrochem.*, **12**, 853, 909 (1906); Seddig, *Sitzb. Naturw. Marburg*, **182** (1907); *Physik. Z.*, **9**, 465 (1908); *Z. anorg. Chem.*, **73**, 360 (1912); Henri, *Compt. rend.*, **146**, 1024; **147**, 62 (1908); de Broglie, *ibid.*, **146**, 624, 1010 (1908); **148**, 1163, 1315 (1909); Seelis, *Z. physik. Chem.*, **86**, 682 (1914).

<sup>2</sup> Perrin, *Ann. chim. et phys.*, **18**, 5 (1909); *Compt. rend.*, **152**, 1380 (1911); Chaudesaigues, *ibid.*, **147**, 1044 (1908); Dabrowski, *ibid.*, **149**, 477 (1909); Bjerrum, *ibid.*, **152**, 1569 (1911).

<sup>3</sup> Svedberg and Inouye, *Arkiv. Kemi Mineral. Geol.*, **4**, No. 19 (1911); Svedberg, *Die Existenz der Moleküle* (Leipzig: Akademische Verlagsgesellschaft m.b.H., 1912); Svedberg and Nordlund, *Z. physik. Chem.*, **87**, 40 (1914).

<sup>4</sup> *Phys. Rev.*, **4**, 440 (1914).

The distribution of displacements observed by Chaudesaigues for gamboge particles in water ( $r = 210 \text{ m}\mu$ ) and by Fletcher for oil drops in air are illustrated in Fig. 3.

(5) **Spontaneous Concentration Fluctuations:** For observation of the spontaneous concentration fluctuations the ultramicroscope is the classical instrument. If attention is focussed upon a small region particles are seen to move into and out of the region as they execute a normal Brownian motion. That is, the number of particles or the concentration in a microscopic volume varies spontaneously and continually on both sides of the mean value. By counting the number of particles every 1.54 sec in a small element of volume optically defined, Svedberg<sup>1</sup> obtained such a series of figures as follows:

. . . 1000322 101230212 1213211101 1002331224 . . .  
2110001203 0101022173 441010 . . .

Although the average concentration was 1.55, momentary values as low as 0 or as high as 7 were observed. Such fluctuations are *apparently*, but not actually, contradictory to the second law of thermodynamics, for a spontaneous increase in concentration or the reversal of diffusion involves a spontaneous decrease in entropy. Superficially the series of numbers appears meaningless, and yet it can be shown to obey a rather elaborate set of laws.

The kinetic and statistical analysis of such fluctuations<sup>2</sup> has been worked out in great detail by von Smoluchowski<sup>3</sup> and in general confirmed by various investigators.<sup>4</sup> If  $\nu$  is the average of the numbers, the difference between any number  $n$  of the series and the average ( $n - \nu$ ) measures the momentary fluctuation, and  $(n - \nu)/\nu$  may be defined as the relative fluctuation  $\delta$ . For an ideal suspension or solution, regardless of whether the kinetic units are molecular or gross particles, the mean relative fluctuation  $\delta$  is given by the equation

$$\delta = \frac{2e^{-\nu}\nu^k}{k!} \quad (5.1)$$

when  $\nu$  is a small number, and  $k$  is the largest integer not exceeding  $\nu$ . The mean square relative fluctuation  $\bar{\delta}^2$  is given by

$$\bar{\delta}^2 = \frac{1}{\nu} \quad (5.2)$$

and the probability for the occurrence of any particular  $n$  is given by the

<sup>1</sup> Svedberg, *Die Existenz der Moleküle*, p. 148.

<sup>2</sup> See Fürth, *Schwankungserscheinungen in der Physik* (Brunswick: Vieweg u. Sohn, 1920), for a general discussion of the topic.

<sup>3</sup> von Smoluchowski, Ostwald's Klassiker, No. 207; *Ann. Physik*, **25**, 205 (1908).

<sup>4</sup> Svedberg, *op. cit.*; Westgren, *Arkiv. Mat. Astron. Fysik*, **11**, Nos. 8 and 14 (1918); **13**, No. 14 (1918); *Z. anorg. Chem.*, **95**, 39 (1916); Costantin, *Ann. phys.*, **3**, 101 (1915); Iljin, *Z. physik. Chem.*, **83**, 592 (1913); Lorenz and Eitel, *Z. anorg. Chem.*, **87**, 357 (1914).

expression

$$P(n) = \frac{n!}{n!} \quad (5.3)$$

Observations by Westgren on a gold sol ( $r = 25 \mu\text{m}$ ) at  $17^\circ\text{C}$  satisfactorily verify these equations (Table III). Using gold particles of radius  $62.5 \mu\text{m}$  Westgren showed in this way that no departure from ideal behavior occurs in concentrations as high as  $72 \times 10^9$  particles per cubic centimeter, corresponding kinetically to  $1.2 \times 10^{-10}$  molar.

TABLE III

SPONTANEOUS FLUCTUATIONS IN CONCENTRATION

 $(\nu = 1.43; \bar{\delta}(\text{obs.}) = 0.70; \bar{\delta}(\text{calc.}) = 0.69; \bar{\delta}^2(\text{obs.}) = 0.74; \bar{\delta}^2(\text{calc.}) = 0.70.)$ 

Momentary concentration $n =$		0	1	2	3	4	5	6	7
Relative frequency $P(n)$	Obs.	381	568	357	175	67	28	5	2
	Calc.	380	542	384	184	66	19	5	2

Von Smoluchowski showed that a discrepancy in these equations may be considered as indicating a condition equivalent to nonideal compressibility in a gas; the "osmotic compressibility"  $\beta$  of colloidal particles may be defined and measured in terms of its ratio to the ideal compressibility  $\beta_0$  by the equation

$$\frac{\beta}{\beta_0} = \left( \frac{\bar{\delta}k!}{2e^{-\nu} \nu^k} \right)^2 \quad (5.4)$$

where  $\nu$  is a small number. For the data of Table III, this ratio is equal to unity within the limits of experimental error, i.e., 1.02, demonstrating that the ideal gas laws are applicable to the colloidal solution investigated. In concentrated gamboge suspensions ( $>2.5$  per cent by volume) Costantin<sup>5</sup> found  $\beta/\beta_0$  to be less than unity; by analogy with the case of a nonideal gas he interpreted this to be due to repulsive forces between the particles.

Von Smoluchowski has also successfully described the speed of concentration fluctuations in terms of the kinetic theory. The speed may be characterized in several ways, among which may be mentioned the following:

(a) The change from one observation to the next, for which the mean-square value is theoretically given by the equation

$$\overline{\Delta^2_n} = 2\nu P \quad (5.5)$$

where  $P$  is a complicated function of the mean square displacement  $\overline{\Delta^2}$ , the time interval between successive observations, and the size and shape of the element of volume in which fluctuations are observed. For special cases of practical importance Westgren has calculated tables of the function, from which

<sup>5</sup> *Compt. rend.*, 158, 1171, 1341 (1914).

he was able to determine the mean-square displacement of particles from the concentration fluctuations and, in turn, the value of Avogadro's constant through Equation (4.6). Some 75,000 values of  $nn_1$  for gold particles of radius  $62.5 \mu$  gave the satisfactory value for  $N$  of  $6.09 \times 10^{23}$ . The frequency of occurrence of any two successive counts  $n$  and  $n_1$  can also be calculated. The first section of Table IV, based upon the same data as Table III, presents a comparison of observed and calculated frequencies.

TABLE IV  
RELATIVE FREQUENCIES OF CONCENTRATIONS  $n$  AND  $n_1$  FOR TWO  
SUCCESSIVE OBSERVATIONS

$n_1 =$		0	1	2	3	4	5	6	7
$n = 0$	Obs.	210	126	35	7	0	1	—	—
	Calc.	221	119	32	6	1	—	—	—
1	Obs.	134	281	117	29	1	1	—	—
	Calc.	119	262	122	31	5	1	—	—
2	Obs.	27	138	108	63	16	3	—	—
	Calc.	32	122	149	63	15	3	—	—
3	Obs.	10	20	76	38	24	6	0	—
	Calc.	6	31	63	56	22	5	1	—
4	Obs.	2	2	14	22	13	11	3	—
	Calc.	1	5	15	22	15	6	2	—
5	Obs.	—	0	2	10	10	1	3	2
	Calc.	—	1	3	5	6	3	1	—

(b) The average duration of a given number  $n$  without change, symbolized by  $T_n$ . Table V contains calculated and observed values from the work of Westgren.

(c) The average interval between two successive occurrences of any given number  $n$ , represented by  $\theta_n$ , for which, also, Table V gives examples. It is interesting to note that the average duration of a state departing widely from the mean does not decrease as rapidly as the frequency with which the wide departure occurs.

Thus, measurements of average displacements and the phenomenon of fluctuations are seen to give a detailed and subtle confirmation of the kinetic theory of dispersed systems, including the underlying assumption of the equipartition of energy between small molecules and gross particles, and the validity of the ideal gas laws applied to suspended particles. With this confidence one may proceed with the more practical methods of osmotic pressure, diffusion, sedimentation, etc., for the determination of particle size and shape.



TABLE V  
 SPEED OF FLUCTUATION

$n =$		0	1	2	3	4	5
$T_n$	Obs.	2.20	1.98	1.43	1.27	1.22	1.08
	Calc.	2.41	1.93	1.63	1.43	1.30	1.21
$\theta_n$	Obs.	6.90	3.53	4.90	9.62	24.6	52.0
	Calc.	7.63	3.71	5.90	10.88	29.9	99.6

(6) **Osmotic Pressure:** If the behavior of colloidal particles is equivalent to that of molecules in an ideal solution, a colloidal solution should display an osmotic pressure in accordance with van't Hoff's laws. As a matter of fact, Einstein<sup>1</sup> showed that the kinetic theory of Brownian motion leads directly to van't Hoff's equation

$$P = nkT \quad (6.1)$$

where  $P$  is the pressure in dynes per square centimeter,  $n$  is the number of particles or molecules per cubic centimeter and  $k$  is Boltzmann's constant. The direct measurement of osmotic pressure with semipermeable membranes is difficult in colloidal systems in which Brownian motion can be observed because of the very low pressures exerted. Observations of changes in vapor pressure, boiling point, or freezing point are also quite impractical.

There has been a sharp revival of interest in studies of the osmotic pressure of solutions of proteins, polysaccharides and their derivatives, dyes, and organic high polymers, substances which in solution give systems intermediate between the classical colloidal and ordinary solutions, in an effort to determine solute molecular weights.<sup>2</sup> With such systems an excessive increase in osmotic pressure with concentration is usually found, the actual variation with concentration being expressed by means of a power series

$$P = Ac_2 + Bc_2^2 + Cc_2^3 + \quad (6.2)$$

The coefficient  $A$  is directly a colligative property, and since the total weight of dissolved material is known it is connected with the molecular weight  $M_2$  of the kinetically active solute. The concentration,  $c_2$ , is in grams per liter. In

<sup>1</sup> *Ann. Physik*, **17**, 549 (1905); **19**, 289, 371 (1906); Ostwald's *Klassiker*, No. 199.

<sup>2</sup> Adair, *Proc. Roy. Soc.*, **A108**, 627 (1925); **109**, 292 (1925); **120**, 573 (1929); **126**, 16 (1929); Pauli and Fent, *Kolloid-Z.*, **67**, 288 (1934); Sørensen, *Z. physiol. Chem.*, **103**, 15 (1918); **106**, 1 (1919); *Kolloid-Z.*, **53**, 102, 170, 306 (1936); Büchner, *Trans. Faraday Soc.*, **29**, 32 (1933); Dobry, *J. chim. phys.*, **31**, 568 (1934); **32**, 50 (1935); *Bull. soc. chim.*, (5) **2**, 1832 (1935); Herz, *Cellulosechem.*, **16**, 56 (1935); Duclaux, *J. chim. phys.*, **28**, 537 (1931); Obogi and Broda, *Kolloid-Z.*, **69**, 172 (1934); Caspari, *J. Chem. Soc.*, **105**, 1239 (1914); Scatchard, *J. Am. Chem. Soc.*, **68**, 2315, 2320 (1946); Fuoss and Mead, *J. Phys. Chem.*, **47**, 59 (1943); Flory, *J. Am. Chem. Soc.*, **65**, 370 (1943).

sufficiently dilute solution, then

$$\lim_{c_2 \rightarrow 0} \frac{P}{c_2} = \frac{RT}{M_2} \quad (6.3)$$

The interpretation of the coefficient  $B$  is more difficult, but it seems proper to assume it results from additional entropy terms and the action of forces between solvent and solute molecules and between solute molecules. A number of investigators<sup>3</sup> have attempted to explain the deviations from the limiting law by the introduction of a co-volume  $b$ , caused by solvation, to give,

$$P_2 \frac{RT}{M} \cdot \frac{1}{V - b} = RT \left( \frac{c_2}{M_2} + bc_2^2 \right) \quad (6.4)$$

Quite satisfactory theoretical treatments of the problem for solutions of linear high polymers have been given,<sup>4</sup> an additional entropy term and an energy term, both proportional to  $c_2^2$ , being described. The partial molal free energy of dilution of the solution,  $\Delta \bar{F}_1$ , is related to the osmotic pressure and partial molal volume of the solvent  $\bar{V}_1$ , by the thermodynamic equation

$$P\bar{V}_1 = -\Delta \bar{F}_1 = T\Delta \bar{S}_1 - \Delta \bar{H}_1 \quad (6.5)$$

Following Huggins, the statistical mechanical treatment for the partial molal entropy of dilution,  $\Delta \bar{S}_1$ , leads to the expression

$$\frac{\Delta \bar{S}_1}{R} = \frac{\bar{V}_1}{\bar{V}_2} V_2 + \left( \frac{1}{2} + \frac{1}{Z'} \right) V_2^2 + \quad (6.6)$$

where  $V_2$  is the volume fraction of solute,  $Z'$  is the effective coordination number of the solvent molecules and solute submolecules and  $\bar{V}_2$  is the partial molal volume of solute. Now, in terms of the interaction constants of solvent and solute  $K_{12}$ , Scatchard<sup>5</sup> has already defined the partial molal heat content of the solvent,  $\Delta \bar{H}_1$  as

$$\Delta \bar{H}_1 = K_{12} \bar{V}_1 V_2^2 \quad (6.7)$$

so that with concentration expressed as grams per liter, of  $c$ , and density of polymer as  $d_2$

$$\begin{aligned} \frac{P}{c_2} &= RT \left[ \frac{1}{M_2} + \frac{1}{d_2^2 \bar{V}_1} \left( \frac{1}{2} - \frac{1}{Z'} - \frac{K_{12}}{RT} \right) c_2 + \dots \right] \\ &= RT \left[ \frac{1}{M_2} + bc_2 + \dots \right] \end{aligned} \quad (6.8)$$

<sup>3</sup> Adair, *loc. cit.*; Burk and Greenberg, *J. Biol. Chem.*, **87**, 237 (1930); **98**, 353 (1932); Stamberger, *J. Chem. Soc.*, 2318 (1928); *Kolloid-Z.*, **53**, 90 (1930); Schulz, *Z. physik. Chem.*, **158**, 237; **159**, 347; **160**, 409 (1932); Sackur, *ibid.*, **70**, 477 (1910).

<sup>4</sup> Kratky and Musil, *Z. Elektrochem.*, **43**, 326, 686 (1937); Flory, *J. Chem. Phys.*, **10**, 51 (1942); Huggins, *J. Am. Chem. Soc.*, **64**, 1712 (1942).

<sup>5</sup> *Chem. Rev.*, **8**, 321 (1931).

Since precise data for the quantity  $\Delta\bar{H}_1$ , to be obtained from a study of the temperature coefficient of osmotic pressure, are not available Huggins makes use of an empirical constant  $\mu$  in the above equation and writes

$$\frac{P}{c_2} = RT \left[ \frac{1}{M_2} + \frac{1}{d_2^2 \bar{V}_1} \left( \frac{1}{2} - \mu \right) c_2 + \dots \right] \quad (6.9)$$

This constant, now a familiar one in high-polymer physical chemistry, is extremely useful in the explanation of solubility relationships in these systems.

For the interpretation of experimental data the Equation (6.3) is quite satisfactory and very practical. In the case of homologous polymers the lines obtained in plots of  $P/c_2$  vs.  $c_2$  form a system of parallel straight lines (slope =  $B$ ) in any one solvent, but if the solvent is changed with any one polymer the intercept on the ordinate (which measures the molecular weight) is unchanged and the slope  $B$  is modified. It is on the basis of this change in slope that a solvent is described as being "good" or "bad."<sup>6</sup> Recognizing that the free energy of dilution is always the same irrespective of the mode of transfer, this equation can be also extended to other phenomena which are intimately related to osmotic pressure sedimentation equilibrium data.

If the colloidal solution contains units of different molecular weight there will be obtained the "number average" molecular weight  $M_n$ , from osmotic pressure studies; thus, if there are  $n_i$  solute molecules (or particles) of mass  $m_i$  per liter so that their concentration (g/l) is  $c_i$ , then

$$M_n = \frac{cN}{n} = \frac{N \sum_i c_i}{\sum_i n_i} = \frac{N \sum_i n_i m_i}{\sum_i n_i} = \frac{\sum_i n_i M_i}{\sum_i n_i} \quad (6.10)$$

Sometimes there is complication due to a pressure exerted by small molecules and ions, which, weight for weight, have a very much greater osmotic activity than the dissolved or suspended colloid.

Since the membranes used with colloidal solutions are usually permeable in some degree to ordinary ions, and the colloid often functions as a "colloidal electrolyte" by giving off or taking on ions, Donnan membrane effects may occur in addition to the membrane difficulties normal to all osmotic pressure measurements. The dependence of the stability of many aqueous dispersions upon the presence of suitable electrolytes often makes it impossible to avoid these effects, and we must consider them here.

(7) **The Donnan Theory of Membrane Equilibria:** Membrane equilibria<sup>1</sup> are usually illustrated by the simplest case, in which two completely dissociated uni-univalent electrolytes, e.g., NaCl and NaX, with a common ion ( $\text{Na}^+$ ) are separated by a membrane that is impermeable to one noncommon ion ( $\text{X}^-$ ).

<sup>6</sup> Alfrey, Bartovics, and Mark, *J. Am. Chem. Soc.*, **64**, 1557 (1942).

<sup>1</sup> Donnan, *Z. Elektrochem.*, **17**, 572 (1911); *Chem. Rev.*, **1**, 73 (1924); *Nat. Research Council Bull.*, No. 69, 51 (1929); Gibbs, *Collected Works* (New York: Longmans, Green and Co., 1931), Vol. I, p. 83; Hückel, *Kolloid-Z.*, **36** (Zsigmondy Festschrift) 204 (1925).

Regardless of the initial conditions, the equilibrium state must meet the thermodynamic criterion that the activities of any diffusible component (solvent and one salt in this case) should be equal on both sides of the membrane; i.e., in the system



the activities at equilibrium must correspond to the equations

$$a_{H_2O}^I = a_{H_2O}^{II} \quad \text{and} \quad a_{NaCl}^I = a_{NaCl}^{II} = a_{Na^+}^I \times a_{Cl^-}^I = a_{Na^+}^{II} \times a_{Cl^-}^{II} \quad (7.1)$$

As an approximation for a dilute solution and complete dissociation, activities may be replaced by stoichiometric concentrations

$$c_{Na^+}^I \times c_{Cl^-}^I = c_{Na^+}^{II} \times c_{Cl^-}^{II} \quad (7.2)$$

The spontaneous maintenance of electroneutrality imposes the additional restriction that

$$c_{Na^+}^I = c_{Cl^-}^I + c_{X^-}^I \quad \text{and} \quad c_{Na^+}^{II} = c_{Cl^-}^{II} \quad (7.3)$$

The combination of these two conditions gives the theoretical description of the membrane equilibrium:

$$\left( \frac{c_{NaCl}^{II}}{c_{NaCl}^I} \right)^2 = 1 + \frac{c_{NaX}^I}{c_{NaCl}^I} \quad (7.4)$$

In other words, since all quantities are positive, the presence of the nondiffusible ion  $X^-$  leads to an unequal distribution of the diffusible ions, the concentration of salt being less in the compartment containing  $X^-$ . Table VI illustrates the

TABLE VI

EFFECT OF A NON-DIFFUSIBLE ION ON THE DISTRIBUTION OF A DIFFUSIBLE SALT  
(SIMPLIFIED THEORY)

Ratio of salt concentration in II to that in I

$c_{NaCl}^I$	$c_{NaX}^I = 0.001$	0.01	0.1	1.0
0.001	1.42	3.32	10.05	31.64
0.01	1.05	1.42	3.32	10.05
0.1	1.005	1.05	1.42	3.32
1.0	1.0005	1.005	1.05	1.42

relations that Equation (7.4) requires between the ratio of salt in compartment II to salt in I and the concentrations of nondiffusible electrolyte and salt in compartment I.

The inequality of the ionic concentrations gives rise to electrical potential differences, the "membrane potentials," which are expressed like those of the

equivalent concentration cells; i.e.,

$$E = -\frac{RT}{F} \ln \frac{c_{\text{Na}^+}^{\text{I}}}{c_{\text{Na}^+}^{\text{II}}} = -\frac{RT}{F} \ln \frac{c_{\text{Cl}^-}^{\text{II}}}{c_{\text{Cl}^-}^{\text{I}}} \quad (7.5)$$

In addition, a difference in osmotic pressures exists in the two compartments. Each pressure is equal to the sum of the partial osmotic pressures of all ionic and molecular species in the compartment, including nondiffusible ions. It is this difference ( $P'$ ) that is measured, rather than the osmotic pressure of the salt  $\text{NaX}$ , whenever diffusible electrolytes are present in the osmosis set-up;  $P'$  is given by the expression

$$\frac{P'}{RT} = 2c_{\text{X}^-}^{\text{I}} + 2c_{\text{Cl}^-}^{\text{I}} - 2c_{\text{Cl}^-}^{\text{II}} \quad (7.6)$$

whereas the osmotic pressure  $P_0$  due to the nondiffusible electrolyte alone is  $2RTc_{\text{X}^-}^{\text{I}}$ . Combining these expressions with the condition for equilibrium, Equation (7.4), and solving for  $P_0$  gives

$$P_0 = P' \left( 1 + \frac{c_{\text{NaCl}}^{\text{I}}}{c_{\text{NaCl}}^{\text{II}}} \right) \quad \text{where} \quad 0 < \frac{c_{\text{NaCl}}^{\text{I}}}{c_{\text{NaCl}}^{\text{II}}} < 1 \quad (7.7)$$

This signifies that when the concentration of diffusible electrolyte is relatively high, e.g., when  $c_{\text{NaCl}}^{\text{I}} = 100c_{\text{NaX}}^{\text{I}}$  and  $\frac{c_{\text{NaCl}}^{\text{I}}}{c_{\text{NaCl}}^{\text{II}}}$  approaches 1, the net osmotic pressure  $P'$  is approximately one-half the partial pressure of the nondiffusible salt, or approximately equal to the pressure of the nondiffusible ion alone. When the concentration of diffusible salt is relatively low, e.g., referring to Table VI, for  $c_{\text{NaX}}^{\text{I}}/c_{\text{NaCl}}^{\text{I}} = 1000$ , the distribution of salt becomes very unequal, and  $P_0$  and  $P'$  approach equality; but even with as high a ratio as this, the discrepancy between  $P_0$  and  $P'$  exceeds three per cent.

The importance of the theory for colloidal behavior arises from the fact that aqueous colloidal solutions normally function as nondiffusible electrolytes. Accordingly, the theory as here sketched has been developed for a number of special cases and made the basis of experimental investigations. Donnan and others<sup>2</sup> have measured the membrane potentials and compared them with values calculated from measurements of the partition of diffusible ions across the membrane. The results on the whole agreed with the simple theory for ideal solutions.

The most important of all osmotic pressures, that of serum albumin under physiological conditions, has been studied by Scatchard<sup>3</sup> and coworkers. The

<sup>2</sup> Donnan and Allmand, *J. Chem. Soc.*, 105, 1941 (1914); Donnan and Garner, *ibid.*, 115, 1313 (1919) (ferrocyanides); Donnan, *Chem. Rev.*, 1, 73 (1924); Loeb, *Proteins and the Theory of Colloidal Behavior* (2d ed.; New York: McGraw-Hill Book Co., Inc., 1924), p. 177 (proteins); Bjerrum, *Z. physik. Chem.*, 110, 656 (1924) (colloidal chromium hydroxide); Rinde, *Phil. Mag.*, 1, 32 (1926) (colloidal sulfur); Northrop and Kunitz, *J. Gen. Physiol.*, 9, 351 (1926) (proteins); Adair, *Proc. Roy. Soc.*, A120, 573 (1928) (hemoglobin).

<sup>3</sup> *J. Am. Chem. Soc.*, 68, 2315, 2320 (1945).

first order Donnan theory for the osmotic pressure of a protein of valence  $z_2$  gives

$$P = \frac{RT}{V_m^0} \frac{w_2}{M} \left( 1 + \frac{w_2 z_2^2}{4 m_3^0 M} \right) \quad (7.8)$$

where  $V_m^0$  is the volume of solution containing 1,000 g of water when  $w_2$  is zero,  $w_2$  is the protein concentration in g per 1,000 g of water,  $m_3^0$  the salt concentration in moles per 1,000 g of water, and  $M$  is the molecular weight of the protein. The difference between the measured osmotic pressure and that calculated from this equation may be used to determine the protein-protein molecule interaction.

The occurrence of Donnan effects is not restricted to systems containing a semipermeable membrane. Whenever the diffusivity of a positive or negative component is spatially restricted in the presence of free ions, a nonuniform distribution of ions and, consequently, osmotic and electrical-potential differences arise: for instance, in a sedimentation equilibrium of a "colloidal electrolyte,"<sup>4</sup> where gravity or centrifugal force substitutes for a membrane in separating the colloidal and ordinary ions; at a surface that dissociates, i.e., possesses a mobile electric double-layer, where the bulkiness and rigidity of the surface, in a sense serving simultaneously as colloidal ion and membrane, restrict the diffusivity of electric charges fixed to it;<sup>5</sup> and in certain permeable solids, like gels, where the gel framework also functions both as colloidal ion and as membrane. The last case is the basis of the Procter-Wilson theory for the swelling of gelatin in the presence of electrolytes (see p. 684), which in turn was shown by Loeb to go far in correlating the effects of electrolytes upon the viscosities of certain protein solutions (cf. p. 685).

(8) **Diffusion:** It is the Brownian motion which is responsible for diffusion. The mathematical relationship between the two phenomena gives what may be termed the general law of the particle. Translational and rotational processes are distinguished in connection with each property.

*Translational Diffusion Constant:* For translational diffusion the first quantitative description was given by Fick,<sup>1</sup> who assumed that the flow of matter in diffusion is entirely analogous to the conduction of heat through a slab, a problem solved by Fourier with the diffusion coefficient taking the place of the thermal conductivity coefficient. Thus, the amount  $dm$  of substance passing through a given area  $a$ , in a short interval of time  $dt$ , and at constant temperature, is proportional to this area and to the concentration gradient  $dc/dx$ , or

$$dm = - Da \frac{dc}{dx} dt \quad (8.1)$$

<sup>4</sup> The term, used here in a more general sense than customary (cf. McBain, in Bogue, *Theory and Application of Colloidal Behavior* (New York: McGraw-Hill Book Co., Inc., 1924), Vol. 1, chap. 16), refers to any system containing a colloidal component that tends to migrate in an electric field.

<sup>5</sup> Michaelis, *Dynamik der Oberflächen* (Dresden: Steinkopf, 1909); *The Effects of Ions in Colloidal Systems* (Baltimore: The Williams and Wilkins Co., 1925); Gouy, *J. phys. rad.*, **9**, 457 (1910); *Ann. physique*, **7**, 129 (1917); Wilson, *J. Am. Chem. Soc.*, **38**, 1982 (1916).

<sup>1</sup> *Phil. Mag.* (4) **10**, 30 (1855).

The constant of proportionality,  $D$ , is the diffusion coefficient of the substance and is expressed in square centimeter per second units. The negative sign indicates that diffusion takes place from a region of higher concentration to one of lower concentration.

A second law of Fick, obtained directly from the first one by a consideration of the relation between  $m$  and  $c$ , is the basis for the present day laboratory determinations of the diffusion coefficient (or constant, as it is usually called). Written in the form

$$\frac{dc}{dt} = D \frac{d^2c}{dx^2} \quad (8.2)$$

it is the most general equation for diffusion in one direction, i.e., along the  $x$ -axis. Obviously it is assumed that  $D$  is here independent of concentration.

Before it can be applied to the practical evaluation of  $D$ , a particular solution must be found which will satisfy the boundary conditions imposed by the experiment. For the diffusion of a solute in a vessel of uniform cross-section from an infinitely long column of solution of concentration  $c_0$  into a similar column of solvent, an experiment ordinarily described as a "blurring of the boundary," we have as solution

$$\frac{c_0}{2} \left( 1 - \frac{2}{\sqrt{\pi}} \int_0^y e^{-y^2} dy \right) \quad (8.3)$$

In this equation  $y = x/2\sqrt{Dt}$ , and  $c$  is the concentration at time  $t$  and distance  $x$  from the initial boundary. The function  $\frac{2}{\sqrt{\pi}} \int_0^y e^{-y^2} dy$  is the probability integral and can be computed from tables; thus the diffusion coefficient  $D$  may be calculated from observations of concentration  $c$ , at different heights  $x$ , after a known time  $t$ .

Actually the better methods for the study of diffusion take advantage of the bending of light by a refractive index gradient in the column to give concentration gradients (page 534), and Equation (8.3) must be differentiated with respect to  $x$  for application. Thus,

$$\frac{dc}{dy} = \frac{-c_0}{\sqrt{\pi}} e^{-y^2} \quad (8.4)$$

$$\frac{dc}{dx} = \frac{dc}{dy} \frac{dy}{dx} = \frac{-c_0}{2\sqrt{\pi Dt}} e^{-x^2/4Dt} \quad (8.5)$$

This equation may be also obtained by the substitution of the general law of the particle  $\bar{\Delta}^2 = 2Dt$  into the Equation (4.7) which gives the probability of the various Brownian displacements. Relative concentrations, Equation (8.3), and concentration gradients, Equation (8.5), as a function of distance in the cell in a diffusion across a boundary are shown in Figs. 4(a) and 4(b), respectively.

Kegeles and Gosting<sup>2</sup> have made a quantitative study of the interference phenomena accompanying the deflection of light by the refractive index gradients in a boundary being blurred by free diffusion. They have established relationships between the spacing of the interference bands and the diffusion constant which will probably revolutionize the experimental determination of diffusion constants.

In certain types of experiment it is important to know how much material has diffused from one layer into another in a given time. Thus, for the case in which the total length of the column  $l$ , is divided into two equal parts, the quantity  $Q$ , which has penetrated into the solvent is obtained by a process of integration.

$$Q = - \int_0^t D \left( \frac{dc}{dx} \right)_{x=l/2} dt \quad (8.6)$$

This equation forms the basis of the so-called porous plate method of Northrop and Anson.<sup>3</sup> The diaphragm separating the two solutions of different concentration is considered to be equivalent to a system of pores with average length  $l$ , and cross-sectional area  $A$ . If the transport of solute takes place solely by diffusion in these pores, the amount  $dQ$  of solute diffusing across the diaphragm in time  $t$  will depend upon the difference in concentration between inner and outer solution,  $c_1 - c_2$ , according to the expression

$$-dQ = DA(c_1 - c_2)dt/l \quad (8.7)$$

The ratio  $A/l$  is determined by a calibration of the cell with a solute of known diffusion constant, the other quantities are measurable to give the coefficient  $D$ .

An additional type of experiment in which material is allowed to diffuse into a porous solid or gel from a stirred solution in contact with it is of considerable chemical interest, but the classical methods of Fourier analysis do not always provide adequate solution of the mathematical problem. March and Weaver,<sup>4</sup>

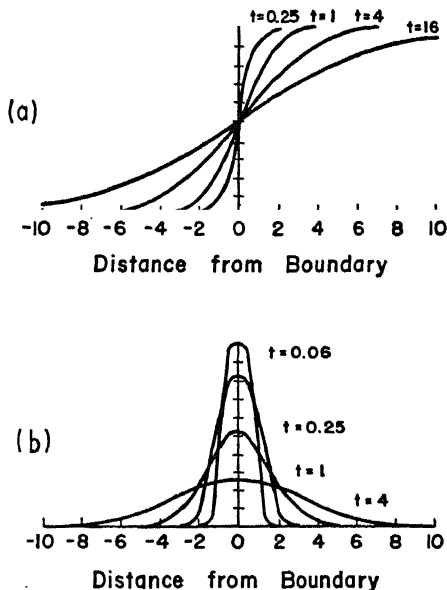


FIG. 4. (a) Relative concentration as a function of distance from solution across boundary into solvent. (b) Concentration gradient as a function of distance from initial boundary. (Adapted from Williams and Cady, *loc. cit.*)

<sup>2</sup> *J. Am. Chem. Soc.*, **69**, 2516 (1947).

<sup>3</sup> *J. Gen. Physiol.*, **12**, 543 (1928); see also Gordon, *Ann. N. Y. Acad. Sci.*, **47**, 285 (1945).

<sup>4</sup> *Phys. Rev.*, **31**, 1072 (1928).



and Langer<sup>5</sup> have discussed this subject in detail to show how a diffusion coefficient may be obtained in experiments of this type.

*Rotary Diffusion Constant:* The study of molecular kinetic properties gives information about the size of macromolecules. In addition to those properties which involve translational motion there are others which have to do with rotational movement. The rotary diffusion constant may be defined by equations analogous to those of Fick for linear diffusion. Corresponding to the first law we have

$$dn = -\theta \frac{d\rho}{d\phi} dt \quad (8.8)$$

where  $dn$  is the number of molecules whose orientation shifts in the time  $dt$  across the angle  $\phi$  from lower to higher values due to the Brownian movement,  $\theta$  is the rotary diffusion constant and  $\rho$  is the direction density, to be compared with concentration, in the system.

In the new terminology the second law becomes

$$\frac{d\rho}{dt} = \theta \frac{d^2\rho}{d\phi^2} \quad (8.9)$$

The rotary diffusion constant  $\theta$  has different physical dimensions from the linear analog  $D$ , its dimensions being simply reciprocal of time.

In general there are two experimental methods which can be used to determine the rotary diffusion constant, but both require systems of a very special kind. The first of these is double refraction of flow. In the theoretical arguments<sup>6</sup> it is supposed that the orienting tendency of the mechanical stresses within the fluid is opposed by the Brownian movement, the disarranging tendency of which is characterized by the rotary diffusion constant  $\theta$ . Thus, if the character of the stresses from the viscous flow in the rotating cylinder instrument is known, and the resulting state of statistical equilibrium between orienting and disorienting tendencies is determined by observations of the double refraction produced, the constant  $\theta$  may be computed. These arguments are limited to thin, rod-shaped molecules for the case of orientation in two dimensions. Edsall<sup>7</sup> has written several review articles in which the theory and its application to give molecular dimension data are discussed.

For some of the proteins it has been found possible to estimate the molecular weights by the study of the dielectric dispersion of their solutions and the application of theory of rotary diffusion.<sup>8</sup> In such cases a finite time is required for the orientation of the molecules in the electrical field owing to the frictional

<sup>5</sup> *Tohoku Math. J.*, **35**, II, 260 (1932).

<sup>6</sup> Boeder, *Z. Physik*, **75**, 258 (1932); *J. Rheology*, **3**, 494 (1932); Kuhn, *Z. physik. Chem.*, **161**, 1 (1932); Haller, *Kolloid-Z.*, **61**, 26 (1932).

<sup>7</sup> Edsall, in *Advances in Colloid Science* (New York: Interscience Publishers, 1942), Vol. I, p. 269; Cohn and Edsall, *Proteins, Amino Acids and Peptides* (New York: Reinhold Publishing Co., 1943), chap. 21.

<sup>8</sup> Williams and Cady, *Chem. Rev.*, **14**, 171 (1934); Williams, *Trans. Faraday Soc.*, **30**, 723 (1934).

resistance of the suspension medium to the rotation; hence, there will be a region in which the dielectric constant of the system decreases as the applied frequency of measurement is increased. The frequency at which the dielectric constant has fallen through one-half of the total drop due to the particular mode of motion is called the critical frequency  $\nu_c$ , and its determination is equivalent to a determination of the rotary diffusion constant  $\theta = kT/\zeta$ ; where  $\zeta$  is a measure of the torque which must be applied to cause the molecule to rotate with unit angular velocity. According to Debye,<sup>9</sup> the frequency  $\nu \cong 1/2\pi\tau$ , where  $\tau$  is the "time of relaxation" of the molecule. For spheres the time constant  $\tau = \zeta/2kT$ , therefore in this case

$$\pi\nu_c = \frac{kT}{\zeta} = \frac{kT}{8\pi\eta r^3} = \theta. \quad (8.10)$$

If, in a given experiment, two relaxation times are found, and they are ideal with respect to the frequency variation of dielectric constant, one may infer the presence either of two spherical molecular species of different size, or of a single species of ellipsoidal molecules having two characteristic axes. Elliott and Williams<sup>10</sup> made a careful study of the second situation in their experiments on the dielectric behavior of solutions of fractionated zein. It was the first time that the dispersion curve for a single molecular species had been unequivocally treated in terms of dipolar motions about different axes of the same molecule. A number of other examples are now known, the work has been extended by Oncley, and the subject has been reviewed by him.<sup>11</sup>

The general subject of molecular diffusion in solution has been reviewed in several places<sup>12</sup> and it is considered unnecessary now to go into further detail.

#### INFLUENCE OF EXTERNAL FORCES UPON KINETIC BEHAVIOR

(9) **Sedimentation Analysis:** Thus far, the application of kinetic theory to colloidal particles and to macromolecular solutions has been considered only for cases in which external influences are absent. However, several cases in which an external force is present are of importance.

In sedimentation analysis, for example, in which gravity or centrifugal force is the external influence, two distinct problems are to be recognized; sedimentation velocity and sedimentation equilibrium. Further, the studies may be carried out with monodisperse systems, paucidisperse systems and polydisperse systems; they will be considered in order. Depending upon the size of the sedimenting particle (or molecule) either the gravitational field of the earth or

<sup>9</sup> Debye, *Polar Molecules* (New York: Chem. Catalog Co., 1929).

<sup>10</sup> *J. Am. Chem. Soc.*, **61**, 718 (1939).

<sup>11</sup> *Chem. Rev.*, **30**, 433 (1942).

<sup>12</sup> Williams and Cady, *Chem. Rev.*, **14**, 171 (1934); Duclaux, *Actualités Scientifiques et Industrielles*, Nos. 349-350 (Paris: Hermann et Cie., 1936); Neurath, *Chem. Rev.*, **30**, 347 (1942); Edsall and Mehl, in Cohn and Edsall *Proteins, Amino Acids, and Peptides*, Longworth, et al., *Ann. N. Y. Acad. Sci.*, **47**, 209-346 (1945); Harned, *Chem. Rev.*, **40**, 461 (1947).

of a centrifuge may be used to cause the redistribution in the system. With a stable or pseudostable colloidal system it will be necessary to make use of centrifugal sedimentation and the instrument for the purpose is now called the "ultracentrifuge," a term first used by Svedberg. In it convection currents (due to temperature differences along the length of the sedimentation column) and vibrations (due to lack of mechanical balance of the rotating part) are eliminated so that the kinetic theory equations are applicable. Furthermore, it is equipped with an optical system such that quantitative observations of the redistribution of the components of a solution or suspension may be made during the progress of a sedimentation.

The first published papers on the ultracentrifuge<sup>1</sup> dealt with analyses of particle size distributions of finely divided materials extending from the finest of inorganic colloids to particles large enough to classify by means of a microscope. As the machines were developed the available centrifugal forces were increased to the point where the smaller proteins could be sedimented with measurable velocities, and it was noted in many cases that all the molecules seemed to sediment at the same rate. In equilibrium determinations with such proteins, the redistribution of solute concentration with distance in the cell follows the well-known hypsometric law. Thus, it is possible, with the centrifugal methods and by making allowance for boundary blurring due to diffusion, to decide whether a dissolved high molecular substance or a colloid is substantially uniform with respect to particle size.

(10) **Sedimentation Velocity:** Sedimentation methods may be conveniently divided into two classes:

(a) Those in which observations are made of the position and shape of a boundary during the sedimentation (boundary method);

(b) Those in which weighings are made of the amount of material thrown out, or accumulated in the bottom of the sedimentation cell (accumulation method).

In general, the boundary methods are used in sedimentation velocity studies with proteins,<sup>1</sup> and the accumulation methods have advantages with inorganic colloids (clays, paint pigments, carbon blacks, etc.).<sup>2</sup>

**Monodisperse Systems:** If the density of a molecule or particle differs from that of the surrounding medium, it will move in a gravitational or centrifugal field at an accelerated rate until the gravitational force equals the frictional force offered by the medium. If  $m$  and  $v$  are the mass and the volume, respectively, of the particle, the actual gravitational force equals  $v(d_p - d)g = m(1 - Vd)g = m_e g$ , where  $d_p$  and  $d$  are the densities of particle and solution,  $g$  is the acceleration of gravity,  $V$  is the partial specific volume of the particle, and with the correction of buoyancy  $m_e$  is the effective mass of the particle.

<sup>1</sup> Svedberg and Nichols, *J. Am. Chem. Soc.*, **45**, 2910 (1923); Svedberg and Rinde, *ibid.*, **46**, 2677 (1924).

<sup>2</sup> Svedberg and Pedersen, *The Ultracentrifuge* (New York: Oxford University Press, 1940).

<sup>2</sup> Tiselius, Pedersen, and Svedberg, *Nature*, **140**, 848 (1937).

The opposing force, which limits the sedimentation rate, is due to viscous friction of the medium to the motion of the particle and is given by  $f(dx/dt)$ , where  $f$  is the frictional coefficient and  $dx/dt$  is the velocity of motion.

When the two forces become equal, the velocity  $dx/dt$  reaches a constant terminal value, and if this is sufficiently low, so that there is no turbulence, we have

$$v(\bar{d}_p - \bar{d})g = m(1 - V\bar{d})g = f \frac{dx}{dt} = m_e g \quad (10.1)$$

and  $(dx/dt)/g = m_e/f = s$ , the "sedimentation constant." The criterion of sufficiently slow velocity is that the Reynold's number,  $\frac{2r\bar{d}x/t}{\eta} < 0.1 - 0.2$  where  $r$  is the effective radius of the particle.

For sedimentation in the ultracentrifuge, the acceleration in the earth's gravitational field ( $g$ ) is replaced by the centrifugal acceleration  $\omega^2 x$ , where  $\omega$  is the angular velocity of the rotor in radians and  $x$  is the distance of the particle from the center of rotation, or on integration,  $x_1$  and  $x_2$  are the distances from the axis of rotation to the boundary at the times  $t_1$  and  $t_2$ , respectively; hence,

$$s = \frac{dx}{dt} / \omega^2 x = \frac{\ln(x_2/x_1)}{\omega^2(t_2 - t_1)} \cong \frac{2(x_2 - x_1)}{(x_2 + x_1)\omega^2(t_2 - t_1)} \quad (10.2)$$

The sedimentation constant is the sedimentation velocity per unit force field; it is a constant characteristic of the sedimenting unit, and it depends upon the size, shape and extent of solvation of this unit, and the viscosity and density of the medium in which the sedimentation takes place. It has the dimensions of time, and is usually expressed in centimeters per second per unit force field for a process taking place in a medium which has the same viscosity and density as water at 20°C, or

$$s_{20} = s \frac{\eta}{\eta_{20}} \frac{(1 - V_{20}\bar{d}_{20})}{(1 - V\bar{d})} \quad (10.3)$$

where  $\bar{d}$  and  $\eta$  are density of solution and viscosity of medium at temperature of the experiment,  $V$  is the partial specific volume of the solute, and  $\bar{d}_{20}$ ,  $\eta_{20}$ , and  $V_{20}$  are the corresponding quantities for water at 20°C. The sedimentation constant is commonly expressed in Svedberg units (S), in which a velocity of  $1 \times 10^{-13}$  cm/sec/unit field = 1 S.

In terms of  $N$  particles or molecules,

$$M(1 - V\bar{d})\omega^2 x = Nf \frac{dx}{dt} \quad (10.4)$$

and since  $f = RT/DN$ ,

$$M = \frac{RT}{(1 - V\bar{d})\omega^2 x} \frac{dx}{dt} \quad (10.5)$$

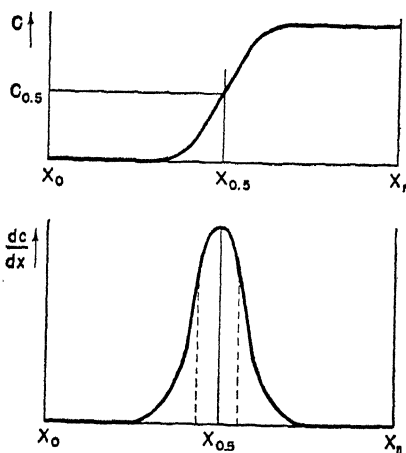
This is one of two fundamental formulae for the calculation of molecular weights from sedimentation data, but it involves the independent determination of the diffusion constant  $D_{20}$  to eliminate the effect of molecular shape.

To observe the changes which take place in the ultracentrifuge cell during the progress of an experiment photographic methods are indispensable. The light-absorption method developed to a high degree of precision by Svedberg<sup>3</sup> and associates to give concentration as a function of distance in the cell is now obsolete. It has been replaced by one of the refraction methods.

Gouy<sup>4</sup> was the first to suggest the use of the bending of light rays in the refractive index gradient in the diffusion column for the determination of the concentration distribution. The first

quantitative work on diffusion with the aid of an optical method was that of Wiener,<sup>5</sup> who also developed the relation between the concentration gradient and the light curvature. The scale method of Lamm<sup>6</sup> in which the displacement of lines in a uniform scale photographed through the cell is determined has been widely used. The cylindrical lens method of Philpot<sup>7</sup> and Svensson<sup>8</sup> and the schlieren-scanning method of Longworth<sup>9</sup> all yield plots of refractive index gradient versus position in the cell directly. A schematic representation of the plots from the light absorption and the refractive index gradient methods is given in Fig. 5.

FIG. 5. Optical Methods for Observing Sedimentation. (a) Plot of concentration versus distance in the cell obtained by the light absorption method. (b) Refractive index gradient, or concentration gradient, obtained by the scale or schlieren methods. (Adapted from Svedberg and Pedersen, *The Ultracentrifuge*).



passes a membrane in a given time. Assuming the solute concentration near the membrane to be constant and the same on both sides, the amount  $dm$  of

<sup>3</sup> Svedberg and Rinde, *J. Am. Chem. Soc.*, **46**, 2677 (1924); Tiselius and Gross, *Kolloid-Z.*, **66**, 11 (1934).

<sup>4</sup> Gouy, *Compt. rend.*, **90**, 307 (1880).

<sup>5</sup> Wiener, *Ann. Physik*, **49**, 105 (1893).

<sup>6</sup> Lamm, *Nova Acta Reg. Soc. Scient. Upsala*, **IV**, 10, No. 6 (1937).

<sup>7</sup> Philpot, *Nature*, **141**, 283 (1938).

<sup>8</sup> Svensson, *Kolloid-Z.*, **87**, 181 (1939).

<sup>9</sup> Longworth, *J. Am. Chem. Soc.*, **61**, 529 (1939); *Ind. Eng. Chem., Anal. Ed.*, **18**, 219 (1946).

substance transported through the membrane in time  $dt$ , is

$$dm = c_t \delta 2\pi x_i \frac{\phi}{360} \omega^2 x_i dt \quad (10.6)$$

where  $c_t = c_0 e^{-2\omega^2 s t}$  the concentration in grams per cubic centimeter at time  $t$ ,  $\phi$  the angle of the sector-shaped cell,  $x_i$  the distance of the membrane from the axis of rotation, and  $\delta$  the thickness of the cell.

After integration, and taking logarithms we have,

$$2\omega^2 t \ln \left( 1 - \frac{m}{c_0 k x_i^2} \right) \quad (10.7)$$

where

$$k = \pi \delta \frac{\phi}{360}$$

In practice, the amount  $Q_t$  of substance present above the membrane after time  $t$  is measured, and

$$- \frac{1}{2\omega^2 t} \ln \left( \frac{x_0^2}{x_i^2} + \frac{Q_t}{c_0 k x_i^2} \right) \quad (10.8)$$

*Paucidisperse Systems:* In the performance of a sedimentation velocity experiment the choice of method of observation of the position of a boundary (or boundaries) as a function of time may depend upon the system being studied. Any modification of the schlieren method may be employed with advantage in the study of a monodisperse system, because of its simplicity. In the case of mixtures of substantially monodisperse systems, called paucidisperse systems, observations of the rate of movement of each boundary are made independently, but the scale method may be superior in that the presence of the several components is observed at a much earlier time, and the sedimentation diagrams give more exact information about the concentration of the several components.

Excellent examples of typical paucidisperse systems are found in blood serum<sup>10</sup> and in some respiratory protein dissociation systems<sup>11</sup>. It will be seen in these reports that although several distinct components happen to be present in the system, each is treated as if it were present alone in the determination of its sedimentation constant.

*Polydisperse Systems:* With the (possible) exception of some crystallizable proteins and certain synthetic products prepared under quite special conditions, macromolecular substances are commonly heterogeneous in molecular weight. Fine powders and colloiddally dispersed material also form polydisperse systems. The only generally applicable methods of determining the degree of heterogeneity of such materials without actually effecting a separation of the material

<sup>10</sup> McFarlane, *Biochem. J.*, 29, 407 (1935).

<sup>11</sup> Svedberg and Pedersen, *The Ultracentrifuge*, 355-372 (New York: Oxford University Press, 1940); Eriksson-Quensel and Svedberg, *Biol. Bull.*, 71, 498 (1936); Svedberg and Eriksson, *J. Am. Chem. Soc.*, 54, 3998, 4730 (1932).

into fractions depend upon sedimentation analysis. For the very finely divided dispersions and for macromolecular substances such analysis requires the application of the ultracentrifuge. Again, there are two distinct methods, one depending upon observations of sedimentation velocity, now to be considered, and the other which involves sedimentation equilibrium.

The fundamental objective of determining size distribution in a solution or suspension is to be able to describe in detail the number of different sizes of macromolecule or particle in a dispersion, and the amounts in each size class. If the suspended units are nonspherical, specification of size and shape characteristics becomes quite complicated, and unless otherwise noted, we shall now restrict ourselves to spherical particles.

Graphical methods of representation of size distributions are normally used. Data are given by *accumulation curves* or by *differential distribution curves*. In the case of the former there is plotted the number of particles smaller (or greater) than a given size against particle radius. Depending upon the use to

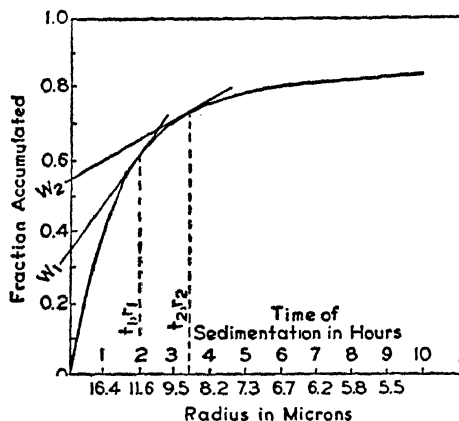


FIG. 6. The Accumulation Curve for the Benzene-Water Emulsion having the Distribution Curve of Fig. 7.\*  $W$ , the weight-fraction deposited, is plotted against time, the corresponding radius being calculated.

\* Kraemer and Stamm, *J. Am. Chem. Soc.*, **46**, 2709 (1924).

which the data are to be put and for any given substance, one may express the abscissae in terms of volume, weight or surface, and the ordinates as per cent of the total volume, or of the total weight, or of the total surface. For example, sieve analysis data are conveniently represented in this fashion.

The differential distribution curve is obtained by plotting the slopes of the accumulation curve at various points against the corresponding radii. On this form of plot, the total area under the curve represents 100 per cent of the material, and the ratio of areas under the curve between any two abscissae to the total area represents the fraction of the material of sizes which fall between

the values of the two abscissae chosen. The maximum of the curve,  $dn/dr$  vs.  $r$  locates the size of the particles present in the greatest number. Again, volume, weight or surface may replace radius. Some experimental techniques give the differential curve directly, so that if the accumulation curve is desired, a process of integration is involved.

There are again the two principal types of sedimentation velocity methods. They are the *deposition* method, and the *sedimentation gradient* method. They have been worked out in detail only for spherical particles showing negligible

diffusivity. When an appreciable fraction of a mixture of many components has a diffusivity which is sufficiently great to broaden its boundary during the course of a sedimentation analysis, it is necessary to take such diffusion into account.

*Deposition Methods (Coarse Dispersions):* When a well-mixed dispersion is allowed to sediment quietly, all the particles of a given size move downward (if  $d_p > d_m$ ) as a group with a constant velocity. Each class therefore accumulates on the bottom at a constant rate (cf. Fig. 6) until the upper boundary of the group, starting from the meniscus, has just deposited—the class of largest particles first, of smallest ones last. Each decrease in the total rate of accumulation of sediment indicates that some size-class has just completed its deposi-

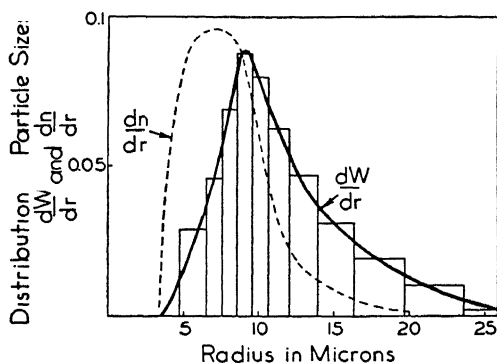


FIG. 7. A Weight-Distribution Curve for the Particle Sizes in a Benzene-Water Emulsion. The dotted curve is the corresponding number-distribution curve obtained by calculation from the weight curve (cf. p. 536). The low-radius portion of such a calculated number-curve is illusory owing to the rapid multiplication of errors as the radius falls below the maximum of the weight curve.

tion. To follow the process, Odén<sup>12</sup> devised an ingenious automatic balance onto one pan of which the sedimenting particles deposited. From a weight-time curve (Fig. 6) a weight-distribution curve (Fig. 7) can be calculated directly.<sup>13</sup>

At time  $t_1$  (Fig. 6) the group of particles having an equivalent radius  $r_1$  (given by Stokes's law where  $t = t_1$  and  $x =$  depth of balance pan from meniscus) just completes its deposition, all larger particles having previously completely deposited; all smaller particles continue to deposit at a rate given by the slope of the tangent at  $t_1$ , as they have done from the beginning of the sedimentation.  $W_1 - w_1$  is therefore equal to the weight of the particles smaller than  $r_1$  that have deposited in time  $t_1$ , and  $w_1$  is the total weight of all

<sup>12</sup> Odén, *Intern. Mitt. Bodenkunde*, 5, 257 (1915). The first arrangement for the purpose, by Schloesing, père, *Compt. rend.*, 136, 1608; 137, 369, 398 (1903), was rather crude and unsatisfactory.

<sup>13</sup> Svedberg, *Colloid Chemistry* (2d ed.; 1928), p. 178.



particles larger than  $r_1$  originally in the dispersion. Similarly for  $t_2$ ,  $w_2$  is the weight of all particles larger than  $r_2$ . Therefore,  $(w_2 - w_1)$  is the weight of particles having a size between  $r_1$  and  $r_2$ , and  $\frac{w_2 - w_1}{r_1 - r_2}$  approaches  $\frac{dW}{dr}$  as  $(r_1 - r_2)$  decreases. The whole curve is treated in this way with a series of short radius intervals. Rectangles of height  $\frac{w_2 - w_1}{r_1 - r_2}$  and of width  $(r_1 - r_2)$  are plotted to give a weight-distribution curve as illustrated in Fig. 7.

Various modifications and improvements in the recording balance have been introduced. The chainomatic principle has been used as well as electromagnetic control by Coutts, Crowther, Keen, and Odén<sup>14</sup> and by Svedberg and Rinde.<sup>15</sup> The latter workers so greatly increased the sensitivity that the total deposit need not exceed 0.02 g.

The expensive and complicated automatic balance may in some cases be replaced by a hand-operated balance<sup>16</sup> or by a simple manometer connected to the side of the sedimentation vessel,<sup>17</sup> the plane at the connecting point being equivalent to a balance pan. As the particles pass this plane, the changes in hydrostatic pressure above it are indicated on the manometer and can be translated into an accumulation curve. The sensitivity has been improved<sup>18</sup> and a photographic recording device<sup>19</sup> added. As the sensitivity is still rather low, dispersions must be of rather high concentration (a few per cent) to be analyzed by the convenient forms of Wiegner's method; however, it is applicable to emulsions with particles sedimenting upwards (cf. Fig. 6).

In any case, the deposition methods in the above forms, using gravity, are limited to fairly large particles, e.g., over 80 m $\mu$  for heavy metals in water, which have an appreciable sedimentation rate and negligible diffusivity. They have been used in the investigation of clays, soils, technical powders such as cements, carbon blacks, and pigments, oil-water emulsions, silver halides for photographic "emulsions," etc.

*Sedimentation-Gradient Methods:* The different rates of sedimentation for the various groups of particles of uniform size produce an echelon grading of the particles in the body of a dispersion (Fig. 8). At any moment the difference in concentration at two adjacent levels equals the concentration in the original dispersion of those size-groups whose top boundaries have settled into this region. The time, the distance of the two levels from the top, and Stokes's law

<sup>14</sup> Coutts, Crowther, Keen, and Odén, *Proc. Roy. Soc.*, **A106**, 33 (1924).

<sup>15</sup> Svedberg and Rinde, *J. Am. Chem. Soc.*, **45**, 943 (1923).

<sup>16</sup> Holmes, *Laboratory Manual of Colloid Chemistry* (2d ed.; New York: John Wiley & Sons, Inc., 1928), p. 10; Börjeson, *Diss.*, Upsala, 1921.

<sup>17</sup> Wiegner, *Landw. Versuchsst.*, **91**, 41 (1918); Kelly, *J. Ind. Eng. Chem.*, **16**, 928 (1924); Stamm, *Colloid. Symp. Monograph*, **2**, 70 (1925).

<sup>18</sup> Hahn, *Z. Elektrochem.*, **27**, 501 (1921), and *Dispersoidanalyse* (Dresden: Steinkopf, 1928); Kelly, *Ind. Eng. Chem.*, **16**, 928 (1924); Kraemer and Stamm, *J. Am. Chem. Soc.*, **46**, 2709 (1924).

<sup>19</sup> Lambert and Wightman, *J. Opt. Soc. Am.*, **11**, 393 (1925); Gessner, *Kolloid-Z.*, **38**, 115 (1926).

permit the calculation of  $r_1$  and  $r_2$ , the radii of the smallest and largest particle in these groups. Analysis gives the two concentrations  $c_1$  and  $c_2$ . A series of the ratios of such pairs  $\frac{c_2 - c_1}{r_2 - r_1}$  may be plotted on a distribution curve (cf. p. 538). Alternatively, the concentration gradient  $dc/dx$  at any level in such a system multiplied by  $dx/dr$ , obtained by the differentiation of Stokes's law and substitution therein with the specific values of  $x$  and  $t$ , gives directly the quantity  $dc/dr$ , which is plotted against the radius of the particles whose top boundary is at the given level. Whenever the dependence of some optical property,

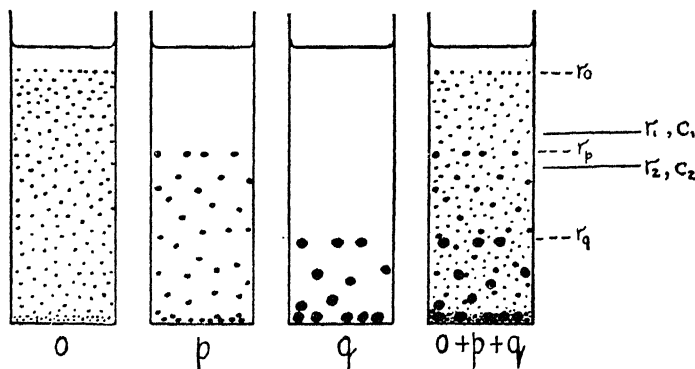


FIG. 8. The Distribution of Three Size-Classes of Particles in a Polydispersed System after a Period of Sedimentation.  $o$ ,  $p$ , and  $q$  give separate views of the different size-classes present in the complete dispersion,  $o + p + q$ .

like absorption<sup>20</sup> or Tyndall effect,<sup>21</sup> upon radius is known, the concentration gradient is easily obtained without disturbing the sedimentation process by direct observation at different levels.

The ultracentrifuge is an ideal instrument for sedimentation analysis, because a very wide range of particle size can be covered by control of speed or of viscosity of dispersion medium or of both. For size distribution measurements, optical analysis is used, with the difficulty that the relation between light absorption coefficient and particle size is not always known. Each increment in light absorption along the column is due to particles of such a size that their boundary occupies the level in question.

Since the field of force is radial, the particles spread apart as they move along radial lines, and the concentration of the body of the suspension falls as it moves downward in the sedimentation cell. Furthermore, since the field increases in proportion to the radius, the particles are separated along a radial line. Both

<sup>20</sup> Svedberg and Rinde, *J. Am. Chem. Soc.*, **45**, 943 (1923), and Rinde, *Diss.*, Upsala, (1928), analyzed various gold sols prepared by the nuclear method.

<sup>21</sup> Svedberg and Stamm, *J. Am. Chem. Soc.*, **47**, 1582 (1925), investigated the influence of various factors upon the degree of dispersion of emulsions by this means.

dilution factors are equal and depend upon the ratio of the radius at the point in question and the radius of the meniscus, i.e.,  $x_t/x_0$ . If, therefore, an increment in concentration is  $c_t/x$  at time of centrifuging  $t$ , the initial or true increment is obtained by multiplying  $c_t/x$  by the correction factors, i.e.,  $c/x = (c_t/x)(x_t/x_0)^2$ . Owing to the fact that light absorption is used,  $kc_t$  and  $kc$  are actually measured. The corresponding  $r$  value is obtained from Stokes's law modified for centrifuge, which may be written in the brief form,  $r^2t = K \ln (x_t/x_0)$ , where  $K$  combines the values for the densities, viscosity of liquid, centrifugal speed, and numerical constants. Upon differentiating this gives

$$\frac{dr}{dx} = \frac{r}{2x_t \ln (x_t/x_0)} \quad (10.9)$$

where  $r$  may be calculated from the form of Stokes's law given above. Therefore,

$$\frac{kc}{r} = \frac{kc}{x} \frac{x}{r} = \frac{kc_t 2x^3 t}{rx_0^2} \ln \frac{x_t}{x_0}$$

These  $\frac{kc}{r}$  values may be plotted against  $r$ .

Some information concerning the polydispersity of a polymer may be obtained also from velocity ultracentrifuge experiments by studying the rate of spreading of the sedimenting boundary.<sup>22</sup>

(11) **Molecular Asymmetry:** Such quantities as the translational and rotational diffusion constants and the specific sedimentation rate are functions of the dimensions of the molecules and the viscosity of the liquid. When the solute molecular weight for a homogeneous substance is known it is possible to calculate what the molar frictional constant ( $f_0$ ) would be for a compact spherical and unsolvated molecule of the same mass. Then

$$f_0 = 6\pi\eta N \left( \frac{3MV}{4\pi N} \right)^{1/3} = \frac{RT}{D_0} \quad (11.1)$$

The actual molar frictional constant as determined by experiment is,

$$f = \frac{M(1 - Vd)}{s} = \frac{RT}{D} \quad (11.2)$$

If the ratio  $f/f_0$  or  $D_0/D$ , known as the dissymmetry constant, is equal to unity for a given substance the molecules must be both spherical and unsolvated. In the case of molecules with dissymmetry constants not much greater than unity, it is impossible to differentiate between a molecule which is spherical and solvated and one which is elongated and unsolvated. This is true because the theoretical coefficient  $f_0$  is calculated from the molecular weight and partial specific volume of the unsolvated molecule, but the measured coefficient  $f$  is

<sup>22</sup> Gralén, *Sedimentation and Diffusion Measurements on Cellulose and Cellulose Derivatives Diss.*, Upsala (1944), p. 18; Kinell, *Acta Chem. Scand.*, 1, 335 (1947).

determined by the solvated molecule of modified partial specific volume and molecular weight. This problem has been discussed at length by Oncley.<sup>1</sup> A ratio greater than 1.5 is usually understood to mean molecular asymmetry, and if it can be assumed that the particles belong to one of a few given simple geometrical types, the frictional ratio may give some information about the molecular shape.

The frictional resistance for prolate and oblate ellipsoids of revolution settling in a viscous liquid was calculated by Gans.<sup>2</sup> The results of these studies were first applied to centrifugal analysis by Rinde,<sup>3</sup> but in making the assumption that the particles were oriented on settling, no allowance was made for the disorientation caused by the Brownian movement. The more complete analysis was made by Herzog, Illig, and Kudar,<sup>4</sup> and by Perrin,<sup>5</sup> whose equations can be written as follows:

*For prolate ellipsoids*

$$\frac{f}{f_0} = \frac{D_0}{D} = \frac{1}{\rho^{2/3} \ln 1 + \sqrt{1 - \rho^2}} \quad (\rho < 1) \quad (11.3)$$

*For oblate ellipsoids*

$$\frac{f}{f_0} = \frac{D_0}{D} = \frac{1}{\rho^{2/3} \tan^{-1} \sqrt{\rho^2 - 1}} \quad (\rho > 1) \quad (11.4)$$

In these formulae  $\rho = b/a$ , where  $b$  is the equatorial radius and  $a$  is one half of the axis of rotation. In computing  $\rho$ , and from it molecular dimensions, from sedimentation and diffusion experiments, as is often done in the case of the proteins, it must be remembered that (1) a molecular shape has been assumed, and (2) no allowance has been made for hydration. The molecular characteristic constants of some proteins are presented in Table VII.

It has been found that molecular asymmetry, molecular weight and relaxation times for a number of proteins are entirely consistent, especially if allowance is made for the effect of hydration. For this purpose, equations of Perrin, relating relaxation time and axial ratio, are used.

The use of viscosity measurements to give information about the shapes of molecules will be considered on page 563. Perhaps a detailed study of flow double refraction should accompany such studies, because by this means information may be obtained concerning the over-all length of the molecule.

The corresponding rotation problems have been also solved; indeed this work preceded treatment of the linear phenomena. The equations are written

<sup>1</sup> *Ann. N. Y. Acad. Sci.*, **41**, 121 (1941).

<sup>2</sup> *Sitz. Ber. Akad. München*, 191 (1911).

<sup>3</sup> *Diss.*, Upsala (1928).

<sup>4</sup> *Z. physik. Chem.*, **167**, 329 (1934).

<sup>5</sup> *J. phys. rad.* (7), **1** (1936).

TABLE VII  
 MOLECULAR CONSTANTS OF SOME SELECTED PROTEINS

Protein		$s_{20}$		$f/f_0$	$M$	$a/b$
Cytochrome C.....	0.707	1.9	10.1	1.2 <sub>4</sub>	15,600	5.2
$\beta$ -Lactoglobulin.....	0.751	3.12	7.3	1.2 <sub>6</sub>	41,500	5.1
Insulin.....	0.749	3.5	8.2	1.1 <sub>3</sub>	41,000	3.3
Ovalbumin.....	0.749	3.55	7.8	1.1 <sub>6</sub>	44,000	3.6
Haemoglobin (horse).....	0.749	4.41	6.3	1.2 <sub>4</sub>	68,000	4.6
Serum Albumin (horse).....	0.748	4.4 <sub>8</sub>	6.1	1.2 <sub>7</sub>	70,000	5.2
Antipneumococcus serum globulin (rabbit).....	0.745	6.5	3.9	1.5 <sub>2</sub>	158,000	9.9
Catalase.....	0.73	11.3	4.1	1.2 <sub>6</sub>	250,000	4.7
Urease.....	0.73	18.6	3.4 <sub>6</sub>	1.1 <sub>9</sub>	480,000	4.0
Antipneumococcus serum globulin (horse).....	0.715	19.3	1.80	1.8 <sub>6</sub>	910,000	19
Erythrocyruorin (Planorbis).....	0.745	33.7	1.96	1.3 <sub>9</sub>	1,630,000	7.3
Haemocyanin (Helix pomatia, main component).....	0.738	98.9	1.38	1.2 <sub>4</sub>	6,600,000	4.6
Tobacco mosaic virus <sup>1</sup> .....	0.73	185	0.53	1.9 <sub>4</sub>	31,600,000	19

$V_{20}$  = partial specific volume

$s_{20}$  = sedimentation constant (in units of  $10^{-13}$  sec, reduced to water at 20°)

$D_{20}$  = diffusion constant (in units of  $10^{-7}$  cm<sup>2</sup> sec<sup>-1</sup>, reduced to water at 20°)

$M$  = molecular weight computed from  $s_{20}$  and  $D_{20}$

$f/f_0$  = ratio of experimentally determined molar frictional constant to molar frictional constant calculated for an unsolvated spherical particle of the same mass

<sup>1</sup> Lauffer, *J. Am. Chem. Soc.*, 66, 1188 (1944).

in terms of the rotary diffusion constants and electrical times of relaxation and may be found in more detailed treatments of the subject.<sup>6</sup>

(12) **Sedimentation Equilibrium: Monodisperse Systems:** In the discussion of the sedimentation velocity problems with the ultracentrifuge it was found that the effect of diffusion sometimes causes difficulty for which allowance must be made, but in the ordinary gravitational cases it is always negligible. On the other hand, in a free diffusion any effect of sedimentation need not be considered. By the use of intermediate gravitational or centrifugal fields in an experiment of sufficiently long duration a state of equilibrium is finally reached in which sedimentation and diffusion balance each other. This means that during the time  $dt$  the quantity  $dn$  of the solute or suspended medium that is driven by the external force through unit surface in the direction of the periphery is equal to that which moves back because of the locally increased osmotic pressure and resultant tendency of the particles to diffuse upward. These two opposing tendencies, regardless of the initial state, eventually give rise to a steady state analogous to that of the atmosphere.

<sup>6</sup> Perrin, *J. phys. rad.*, (7), 5, 497 (1934). See also Cohn and Edsall, *Proteins, Amino Acids and Peptides* (1943), chap. 21.

The number of particles sedimenting per second through unit plane is

$$\left(\frac{dn}{dt}\right)_s = \frac{nm_s g}{f} \quad (12.1)$$

The number of particles diffusing per second through the same plane, in the opposite direction, is

$$\left(\frac{dn}{dt}\right)_D = -D \frac{dn}{dx} = -\frac{kT}{f} \frac{dn}{dx} \quad (12.2)$$

In these expressions  $n$  is the number of particles per cubic centimeter at a given level. At equilibrium these two quantities are equal, and

$$= -kT \frac{dn}{dx} \quad (12.3)$$

Upon integration,

$$\ln n = -\frac{m_s x g}{kT} + \text{const} \quad (12.4)$$

Thus, the logarithm of the concentration is a linear function of the height, and the slope of the line obtained when  $\ln n$  is plotted against  $x$ , the cell height, is  $-m_s g/kT$ . It should be noted that the frictional coefficient  $f$  has been removed by cancellation, so the calculation of the mass  $m$  of a particle gives a value which is independent of shape.

In a centrifugal field the acceleration of the earth's gravitational field  $g$  is replaced by  $\omega^2 x$ , the centrifugal acceleration, and

$$\ln n = \frac{-m_s \omega^2 x^2}{2kT} + \text{const} \quad (12.5)$$

In this instance the plot  $\ln n$  vs.  $x^2$  gives a straight line, with slope  $-m_s \omega^2/2kT$ , from which the mass  $m$  can be calculated. The molecular weight  $M$  is given by the classical equation, obtained by integration between limits,

$$M = \frac{2RT \ln c_2/c_1}{(1 - Vd)\omega^2(x_2^2 - x_1^2)} \quad (12.6)$$

where  $d$  now becomes the density of the solution.

The state of affairs preceding the attainment of equilibrium has been analyzed mathematically.<sup>1</sup> In principle, there is a gradual transition between conditions suitable for observation of sedimentation rate and those for sedimentation equilibrium.

*Polydisperse Systems:* If the suspension is dilute, and contains two or more different sizes, the particles in each size class will attain their own equilibrium distribution. However, the total curve,  $\ln n$  vs. cell height  $x$ , being the sum

<sup>1</sup> Mason and Weaver, *Phys. Rev.*, **23**, 412 (1924); Weaver, *ibid.*, **27**, 499 (1926); Archibald, *Ann. N. Y. Acad. Sci.*, **43**, 211 (1942); *J. Applied Phys.*, **18**, 362 (1947).

of the individual straight lines, will not be a straight line, but will be curved convex to the  $x$ -axis. Thus, a mixture may be recognized at once.

The equilibrium ultracentrifuge is a good instrument for estimating the molecular weights of certain macromolecular materials. Most methods (osmotic pressure, viscosity, end-group titration, and, in actual present day practice, light scattering) do not detect heterogeneity and therefore give average values, which may differ, depending upon the relationship between the measured property and molecular size. Before comparison of results obtained for a given

heterogeneous material by the several methods is possible, consideration must be given to the types of average value which the different methods yield. The advantage of the sedimentation equilibrium method is that all of the common average molecular weights may be obtained from it directly or indirectly.

As already seen, page 524, osmotic pressure depends in principle upon counting the molecules or particles in a sample of given weight to give a number average molecular weight. This will also be true in the case of end-group titration and ultramicroscopic count experiments. The average value from any method depending on the weights of the molecules (light scattering, sedimentation equilibrium by using light

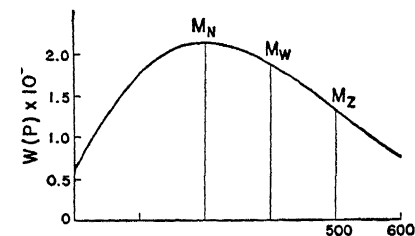


Fig. 9. Molecular Weight Averages.  $W(P)dP$  is the weight fraction of the polymer having a degree of polymerization between  $P$  and  $(P + dP)$ . For a polymer having a Schulz distribution

$$W(P) = \frac{\alpha^P (1 - \alpha)^{b+2} P^{b+1}}{(b+1)!}$$

where  $\alpha = 0.99$ ,  $b = 2.0$ . (Adapted from Singer, *J. Polymer Sci.*, 1, 445 (1946).)

absorption, and viscosity when it is applicable), is called the "weight average" molecular weight, given by the expression

$$M_w = \frac{\sum n_i M_i^2}{\sum n_i M_i} = \frac{\sum c_i M_i}{\sum c_i} \quad (12.7)$$

Sedimentation equilibrium in the ultracentrifuge yields, under favorable conditions, number-average and weight-average molecular weights, and, in addition, "z-average"<sup>2</sup> and even higher moment molecular weights. The z-average molecular weight is defined as

$$M_z = \frac{\sum n_i M_i^3}{\sum n_i M_i^2} = \frac{\sum w_i M_i^2}{\sum w_i M_i} \quad (12.8)$$

<sup>2</sup> The term z-average seems cumbersome, but since it is the result obtained directly from the usual refractive-index records of sedimentation equilibrium we shall retain it. Actually it might be called the third moment molecular weight, meaning thereby the ratio of the third moment to the second moment of the number-distribution curve. Thus, number and weight averages are first and second moment molecular weights, respectively.

It is commonly obtained in experiments where scale optical systems are used to study the redistribution of components in the cell. Therein lies a great potential advantage of this method, because the relationship between the molecular weights of successively higher moment gives one means of study of the size distribution. This point may be illustrated by Fig. 9 in which are indicated the several average molecular weights in a polymer system for which the Schulz distribution of size function is assumed.

Rinde <sup>3</sup> has discussed this problem in considerable detail, and has described two methods for determining a size-distribution relationship that would give the observed sedimentation equilibrium in ideal solutions. The first method involves the solution of a series of simultaneous linear equations of  $n$  unknowns, where  $n$  is equal to the number of particle-size classes assumed to be present in the mixture. As Rinde has shown, the total concentration  $c_x$  at the point  $x$  in the sedimentation equilibrium is equal to the sum of the contributions made by the  $n$  molecular species or particle-size classes in the mixture, i.e., for a sector cell

$$c_x = \sum_{i=1}^{r=n} c_{r_i} \frac{B(b^2 - a^2)e^{-B(b^2 - x^2)}}{1 - e^{-B(b^2 - a^2)}} \quad (12.9)$$

where

$$B = \frac{2N\pi r^3(d_p - d_m)\omega^2}{3RT} \quad (12.10)$$

and  $c_{r_i}$  is the concentration of the  $i$ th size-class in the mixture. With  $n$  or more experimental values of  $c_x$ , the system of equations is solved for the  $c_{r_i}$  values, which are required for the construction of the size-distribution curve. In practice, however, Rinde reported this method to be unsatisfactory owing to the effects of unavoidable experimental errors, some negative values for  $c_{r_i}$  usually being obtained. This method would probably be most satisfactory for mixtures containing only a few discrete and well-separated size-classes of known particle size.

Rinde's second method, which he called the "integral method," involved the use of a complicated polynomial and laborious calculations, and is therefore not suitable for general use.

More recently Wales <sup>4</sup> has returned to this general problem of obtaining information about the molecular weight distribution, for example, in a polymer system. But before turning to this development mention should be made of the Lansing-Kraemer <sup>5</sup> approach in which an empirical distribution function characterized by a limited number of parameters is selected and fitted to the observed results. In practice the three (or four) average molecular weights which are available are used with a logarithmic number distribution which may

<sup>3</sup> *Diss.*, Upsala (1928).

<sup>4</sup> *J. Phys. Colloid Chem.*, **52**, 235 (1948); Wales, Williams, Thompson, and Ewart, *ibid.*, **52**, 984 (1948).

<sup>5</sup> Lansing and Kraemer, *J. Am. Chem. Soc.*, **57**, 1369 (1935).



be written

$$dn = \frac{N}{\sqrt{\pi}} e^{-y^2} dy \quad \text{where} \quad y = \frac{1}{\beta} \ln \frac{M}{M_0} \quad (12.11)$$

On a weight basis we have,

$$dw = \frac{W}{M_n \beta \sqrt{\pi}} e^{-y^2} dM \quad (12.12)$$

where  $N$  and  $W$  represent total number and weight of particles,  $M_0$  is the molecular weight belonging to the maximum in the weight distribution curve, and  $\beta$  is the non-uniformity coefficient. Corresponding to this distribution,

$$M_0 = M_p e^{0.5\beta^2}, \quad M_n = M_p e^{0.75\beta^2}, \quad M_w = M_p e^{1.25\beta^2}, \quad \text{etc.} \quad (12.13)$$

where  $M$  is the maximum of the  $dn/dM$  vs.  $M$  curve, that is, the most probable molecular weight. The Lansing-Kraemer treatment involves the use of two parameters.

If an attempt is made to fit a generalized many-parameter curve to a set of moments the labor may be great, and Wales <sup>6</sup> has argued that it is just as easy to solve the integral equation of sedimentation equilibrium; so, it seems likely that his type of analysis will replace the empirical treatment of Lansing and Kraemer.

A detailed study of the application of the Wales method to polystyrene systems has been made.<sup>7</sup>

(13) **Ultracentrifuges:** The equations given above and others derived from or related to them form the basis for the powerful ultracentrifugal methods of investigating the dispersity of colloidal solutions, which have been so brilliantly developed in recent years by Svedberg and his associates.<sup>1</sup> In these centrifuges phenomena occur in highly dispersed or even molecular systems on the same scale as in coarse dispersions under the influence of gravity; moreover they can be quantitatively observed or recorded while the centrifuges are in operation.<sup>2</sup> Again we distinguish between sedimentation velocity and sedimentation equilibrium experiments because the equipment required in the cases will be different. The ingenious experimental arrangements are in themselves of considerable interest and variety. Sedimentation velocity analytical centrifuges may be driven by oil <sup>3</sup> by air <sup>2</sup> and by electricity,<sup>4</sup> but the only successful sedimentation equilibrium instrument, that of Svedberg, is driven from the shaft of an electric motor.

<sup>6</sup> *J. Phys. Colloid Chem.*, **52**, 235 (1948).

<sup>7</sup> Wales, Williams, Thompson, and Ewart, *J. Phys. Colloid Chem.*, **52**, 984 (1948); Thompson, *ibid.*, **54**, 338 (1950).

<sup>1</sup> Svedberg and Pedersen, *The Ultracentrifuge* (1940).

<sup>2</sup> Pickels and Beams, *Science*, **81**, 342 (1935); Bauer and Pickels, *J. Exp. Med.*, **64**, 503 (1936); **65**, 565 (1937).

<sup>3</sup> Svedberg and Pedersen, *op. cit.*

<sup>4</sup> Beams and Snoddy, *Science*, **85**, 185 (1937); Beams, *Rev. Mod. Phys.*, **10**, 245 (1938).

The standard Svedberg oil-turbine ultracentrifuge gives centrifugal forces in the practical range from 18,000 to 350,000 times gravity. The rotor of chrome nickel steel is supported in horizontal bearings and driven by twin oil-turbines on each end of the main shaft. In operation the solution is placed in a small cell inserted in the rotor. The cell has transparent windows, and in the heavy steel chamber which encloses the rotor there are windows in the optical path which are opened and closed with electromagnetic shutters. By directing a beam of light through the cell the progress of sedimentation may be observed.

Due to the persistence of vision, an apparently continuous view of the rotating cell and its contents may be had through these windows. Two different properties of the solute may be utilized for the determination of its redistribution in the cell, the light absorption and the light refraction. It is the refraction methods which are now almost universally used. They may involve the photography of a uniform linear scale through the sedimentation system or they may consist of one of the so-called "schlieren" systems. In addition to its well-known success as an instrument for observations of sedimentation velocity the high speed oil-turbine ultracentrifuge has been found to be practical in sedimentation equilibrium studies of molecules as small as urea.

There are two kinds of high speed air-driven centrifuges, one of which, the suspended rotor vacuum-type, has been successful as an analytical tool. Here, the rotor spins in a vacuum on a flexible vertical shaft, thus eliminating the troublesome effects of air friction. Exclusive of the optical system and cell which are similar in plan to those used in oil driven assemblies, this machine consists of a Duralumin rotor located inside a vacuum-tight chamber, a small air-driven and air-supported turbine and a flexible wire shaft which fastens them together and which is coaxial with their common axis of rotation. The "spinning-top" variety of air-driven centrifuge is a most useful laboratory tool for the concentration and purification of some biologically interesting and active materials, such as viruses, but it has not been in general use as an analytical instrument for the determination of sedimentation velocities. The expanding air jets which impinge upon the under surface of the rotor cool it, while the air friction around the periphery on the top of the rotor causes heating so that convection-free sedimentation is impossible of achievement in any of the simple forms.

Perhaps the velocity ultracentrifuge of the future will be driven by electricity—at least an auspicious start in this direction has been made.<sup>5</sup> It seems fairly obvious that a system with electrical drive but which at the same time embodies the desirable characteristics of the air-driven, vacuum-type centrifuge would have great practical utility. The chief differences are that an electrical motor is substituted for the air drive and a magnetic support is used instead of an air-lift. The field coils of the driving motor are supplied with a high-frequency alternating current in such a way that the field rotates with the same frequency as the alternating current. The rotating field induces currents in

<sup>5</sup> Skarston and Beams, *Rev. Sci. Inst.*, 11, 398 (1940).

the solid steel armature, causing it to rotate, and along with it the rotor suspended from it. In this way the speed is subject to delicate and accurate control. Even more recently Pickels and his associates have developed an instrument, the rotor of which is driven by gears from the shaft of an electric motor.<sup>6</sup> This instrument is now rather widely used in American research laboratories.

The Svedberg equilibrium ultracentrifuge is driven directly from the shaft of an electric motor with speeds up to 18,000 rpm. The rotor is placed in a water-tight housing, thermostated on the outside. Hydrogen at atmospheric pressure flows through the housing to increase thermal conductivity. It is a useful machine for sedimentation equilibrium measurements with solutions of many organic macromolecules and for sedimentation velocity measurements with most inorganic colloids. When density and size of macromolecule are favorable velocity determinations are also possible with the machine.

### OPTICAL PROPERTIES OF COLLOIDAL SOLUTIONS

(14) **Color:**<sup>1</sup> The variety and intensity of color of colloidal solutions have attracted attention. Gold hydrosols may be ruby red, various shades of violet, or blue; Carey Lea's silver sols are yellow in all shades to brown, bright red, dark red, violet, greenish blue, olive green, or black; ether sols of sodium, potassium, rubidium, and cesium vary in color from violet to bluish green, resembling the corresponding vapor colors. The colors persist in extraordinarily high dilutions;<sup>2</sup> the color of colloidal arsenic trisulfide is detectable in more than 10<sup>6</sup> parts of water, colloidal ferric hydroxide has several times the color intensity of ferric thiocyanate, and colloidal gold possesses a detectable color in about 500 times as great a dilution as ionic gold. The color of a sol may change under the influence of specific agencies; for instance, the addition of a small quantity of common salt to a red gold sol converts it to a blue one.

These manifestations show that the color and condition of the colloidal material are intimately related. Efforts have not been lacking to provide a rational interpretation of the phenomena. Color in colloidal systems may be caused by scattering from small particles, interference, diffraction, refraction and absorption. Using the absorption coefficient and refractive indices measured on bulk gold, Mie<sup>3</sup> calculated the absorption curve that a dispersion of very small gold spheres should show, and in approximate agreement with

<sup>6</sup> Pickels, in Alexander, *Colloid Chemistry* (New York: Reinhold Publishing Corporation, 1944), Vol. V., p. 411.

<sup>1</sup> General references: Bancroft, *Applied Colloid Chemistry* (1926), p. 238, and numerous articles in *J. Phys. Chem.*; R. Gans, *Lichtzerstreuung*, in Wien-Harms, *Handb. Experimental Physik* (Leipzig: Akademische Verlagsgesellschaft m.b.H., 1928), Vol. 19, p. 363; W. Ostwald, *Licht und Farbe in Kolloiden* (Dresden: Steinkopf, 1924), a detailed summary of work antedating 1914; Wood, *Physical Optics* (New York: The Macmillan Company, 1911), chap. 22.

<sup>2</sup> Svedberg, *Kolloid-Z.*, 4, 168 (1909); 5, 318 (1910); *Z. physik. Chem.*, 67, 249 (1909); *Die Existenz der Moleküle* (Leipzig: Akademische Verlagsgesellschaft m.b.H., 1912).

<sup>3</sup> *Ann. Physik*, 25, 377 (1908); Maxwell Garnett, *Phil. Trans. Roy. Soc.*, 203, 385 (1904); 205, 237 (1906); Lange, *Z. physik. Chem.*, 132, 27 (1928).

experiment,<sup>4</sup> he found a pronounced absorption maximum in the green, corresponding to the actual red color by transmitted light. With increasing radius the theory indicated a shift in the absorption maximum toward greater wavelengths, producing bluish-red, violet, and blue colors, as actually occurs in certain gold sols. Sols ordinarily contain many sizes of particles, and in addition, the particle shape and structure and the surface composition are undoubtedly more complicated than assumed. Color and absorption are sensitive indicators of differences in the physical structure of dispersions, but they do not always yield definite conclusions concerning the exact nature of the differences.

(15) **The Tyndall Effect:**<sup>1</sup> Faraday<sup>2</sup> noticed that the path of a narrow beam of sunlight passing through a colloidal gold solution was plainly visible when examined against a dark background although the sol appeared quite transparent under the microscope. He suspected that very small particles of gold were responsible for the light emitted or "scattered" by the solution laterally to the incident beam. In the course of a detailed examination of the effect, Tyndall<sup>3</sup> took note of the blue color and polarized character of the scattered light and the yellowish-red color of the transmitted light for dispersions of transparent materials. This capacity to scatter light, usually called the "Tyndall effect," is now recognized to be a general property of matter that is particularly marked in colloidal solutions.

The first successful mathematical analysis of the Tyndall effect was carried out by Lord Rayleigh,<sup>4</sup> who calculated the theoretical relationship for very small nonconducting particles between the intensity  $I$  of the scattered light at a distance  $x$  from the specimen and the intensity  $I_0$  of the incident light, the number of particles per unit volume  $\nu$ , their volume  $v$  and the index of refraction  $n_1$ , the wavelength of the unpolarized incident light  $\lambda$ , the refractive index of the medium  $n$ , and the angle between the incident beam and the direction of observation  $\theta$ ; thus,

$$I = I_0 \frac{9\pi^2 v^2 n^4 \nu (n_1^2 - n^2)^2}{2x^2 \lambda^4 (n_1^2 + 2n^2)} (1 + \cos^2 \theta) \quad (15.1)$$

The fourth power of the wavelength indicates the more effective scattering of the shorter waves, which accounts for the bluish Tyndall beam in dispersions of colorless substances when the incident light is white. It is evident that there

<sup>4</sup> Steubing, *Ann. Physik*, **26**, 329 (1908). Observations by Pihblad, *Diss.*, Upsala, 1918, and by Rinde, *Diss.*, Upsala, 1928, on gold sols agree with theory to ca. 10–25 per cent.

<sup>1</sup> General reviews: Wells, *Chem. Rev.*, **3**, 331 (1927); Freundlich, *Colloid and Capillary Chemistry* (New York: Dutton, 1926), p. 379; Ostwald, *Licht und Farbe in Kolloiden* (Dresden: Steinkopf, 1924).

<sup>2</sup> *Phil. Trans. Roy. Soc.*, **147**, 154 (1856).

<sup>3</sup> *Phil. Mag.*, **37**, 384 (1869).

<sup>4</sup> *Ibid.*, **47**, 375 (1899).

\* Sinclair and La Mer [*Chem. Rev.*, **44**, 245 (1949)], and Sinclair [*J. Optical Soc. Am.*, **37**, 475 (1947)] have shown that the value usually given in the literature for the intensity scattered by particles illuminated by unpolarized light is too large by a factor of 2 because of a mistake originally made by Rayleigh.

can be no scattering unless the refractive indices of particle and medium differ. The distribution of the scattered light and its state of polarization are contained in the  $(1 + \cos^2 \theta)$  term and can be graphically represented by a polar diagram resembling that of Fig. 10, but with  $i_1$  as a circle and  $i_2$  as a symmetrical  $\cos^2 \theta$  curve about the particle as center. The lengths of the radii from the particle to the curves are proportional to the intensities of the two polarized components of the scattered light,  $i_1$  for the component vibrating perpendicular to the plane containing the incident beam and the direction of observation, and  $i_2$  (propor-

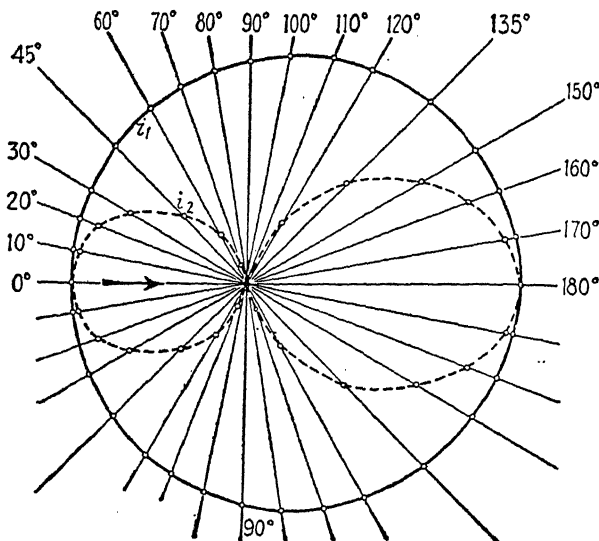


FIG. 10. Theoretical Polarization and Relative Intensity of Light Scattered by a Flint Glass Particle (radius = 50  $m\mu$ ; refractive index = 1.67) in Water. The arrow indicates the direction of the incident non-polarized light, which is about 300 times as intense as the light scattered at 180°.

tional to  $\cos^2 \theta$ ) for the component at 90° to  $i_1$ . The total intensity in any direction is given by the sum of  $i_1$  and  $i_2$  along any radius vector, and the net intensity of the polarized light is proportional to the difference between  $i_1$  and  $i_2$ . At 90°, the scattered light is polarized completely in the absence of secondary scattering.

The Rayleigh formula has frequently served as a starting point for investigations of dispersions. Considering all variables except concentration and particle size to be constant, Equation (15.1) may be rewritten in the form  $I = kcv^2$  where  $k$  is an unknown constant of proportionality,  $c$  is the concentration, and  $v$  is the average volume of the particles. Therefore, by means of measurements of relative Tyndall intensities of dispersions of the same kind and size of particle, relative concentrations can be estimated, as in nephelometry;<sup>5</sup>

<sup>5</sup> Yoe, *Photometric Chemical Analysis*, Vol. 2, *Nephelometry* (New York: John Wiley & Sons, Inc., 1929).

or differences in particle size can be estimated by the comparison of dispersions of a given material in equal concentrations. This principle has been applied in numerous investigations of degree of dispersion and of the effects of time, added agents, and external conditions upon colloidal systems.

When a ray of white light is passed through a monodispersed colloid, in which the radius of the dispersed particles is of the order of magnitude of the wavelength of the light and the indices of refraction of the dispersed and continuous phases differ appreciably, the color of the scattered light depends upon the angle of observation. This effect which was observed by Ray<sup>6</sup> may be designated as the higher order Tyndall spectra.

**(16) Application of Light-Scattering Methods to Particle Size Determination:** The simple theory of Rayleigh is applicable only to the case of very dilute suspensions of small isotropic spherical particles where  $r \leq \lambda/20$ . The theory of Gans<sup>1</sup> extends this treatment to dilute solutions of nonspherical particles of almost any regular shape, but still carries the restriction  $r \leq \lambda/20$ . The Mie theory applies to dilute systems of spherical isotropic particles of any size. Debye<sup>2</sup> has shown that by treating the effect of the molecular inhomogeneities on the light in a second approximation as due to spontaneous fluctuations of the density and the concentration in a medium which in a first approximation is considered to be perfectly homogeneous,<sup>3</sup> the intimate connection between light scattering and osmotic pressure is revealed, and the effects of concentration on osmotic pressure and on light scattering can be related to each other. This theory has the important advantages of applying to nonspherical particles and more concentrated solutions, but it is restricted to particles small compared to the wavelength of light.

Even nonabsorbing liquids are not perfectly transparent, but scatter light. The main part of this light has not changed its wave length (Raman effect), but is scattered by the nonhomogeneous molecular structure of the liquid. We would expect if a solvent is made more inhomogeneous by adding a solute the scattered intensity would increase.

The spontaneous fluctuations in concentrations are smaller in magnitude the larger is the osmotic work performed in causing the change in concentrations. The Einstein theory relates the intensity of scattering to the change in refractive index, and therefore to the change in concentrations which is its cause. The relation is

$$\tau = \frac{32\pi^3}{3} \frac{n_0^2}{N\lambda^4} \frac{(cdn/dc)^2}{c\partial(P/RT)/\partial c} \quad (16.1)$$

where  $\tau$  is the turbidity (extinction coefficient in  $\text{cm}^{-1}$  due to concentration fluctuations),  $n$  the refractive index ( $n_0$  for the solvent),  $\lambda$  the wavelength of

<sup>6</sup> *Indian Assoc. Cult. Sci.*, 7, 1 (1921).

<sup>1</sup> *Ann. Physik*, 37, 881 (1912).

<sup>2</sup> *J. Applied Phys.*, 15, 338 (1944); *J. Phys. and Coll. Chem.*, 51, 18 (1947).

<sup>3</sup> See fluctuation treatment of Smoluchowski, *Ann. Physik*, 25, 205 (1908); Einstein, *ibid.*, 33, 1275 (1910).

incident light,  $c$  the concentrations in grams per ml, and  $P$  the osmotic pressure. This equation is commonly written as

$$H \frac{c}{\tau} = \frac{\partial}{\partial c} \left( \frac{P}{RT} \right) \quad (16.2)$$

where  $H$ , called the refractive constant, is given by

$$H = \frac{32\pi^3 n_0^2}{3 N\lambda^4} \left( \frac{n - n_0}{c} \right)^2 \quad (16.3)$$

Since, as seen earlier, the osmotic pressure of a high polymer solution may be expressed adequately by a two-term expansion of the form

$$\frac{P}{RT} = \frac{c}{M_2} + Bc^2 \quad (16.4)$$

we have to expect, according to Equation (16.2), the linear relationship

$$H \frac{c}{\tau} = \frac{1}{M_2} + 2Bc \quad (16.5)$$

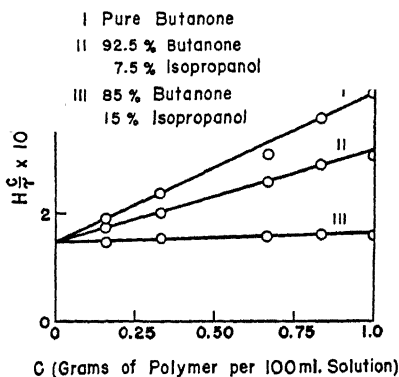


FIG. 11. Light Scattering Curves for Fractionated Polystyrene. (Ewart, Roe, Debye, and McCartney, *loc. cit.*)

of refractive index as they change with concentration. Such a plot is shown in Fig. 11.<sup>4</sup>

If the macromolecular long dimensions extend beyond a few hundred Å, the angular intensity of the scattered light is no longer symmetrical about 90°, and from observations of the angular variation in intensity it is possible to obtain information about the length of the molecule and some idea as to its rigidity.<sup>5</sup>

In the case of spherical particles which are large compared to  $\lambda$ , such as the particles of sulfur sols<sup>6</sup> and oil fogs,<sup>7</sup> the Mie theory provides a method for the

<sup>4</sup> Zimm and Doty, *J. Chem. Phys.*, **12**, 203 (1944); Doty, Zimm, and Mark, *ibid.*, **13**, 159 (1945); Zimm, *ibid.*, **13**, 141 (1945); Heller and Klevens, *Phys. Rev.*, **67**, 61 (1945); Ewart, Roe, Debye, and McCartney, *J. Chem. Phys.*, **14**, 687 (1946); Zimm, Stein, and Doty, *Polymer Bull.*, **1**, 90 (1945).

<sup>5</sup> Stein and Doty, *J. Am. Chem. Soc.*, **68**, 159 (1946); Oster, Doty, and Zimm, *ibid.*, **69**, 1193 (1947).

<sup>6</sup> LaMer and Johnson, *J. Am. Chem. Soc.*, **67**, 2055 (1945); **69**, 1184 (1947); LaMer and Barnes, *J. Colloid Sci.*, **1**, 77, 79 (1946).

<sup>7</sup> Sinclair and LaMer, *Chem. Rev.*, **44**, 245 (1949).

determination of particle size. According to the theory, the intensity of unpolarized light scattered in the direction  $\gamma$  by spheres of any size is

$$I_{\gamma} = \frac{\lambda^2}{8\pi^2 x^2} (i_1 + i_2) \quad (16.6)$$

where the angular distribution functions  $i_1$  and  $i_2$  are complicated functions of the index of refraction,  $\lambda$ , particle size, and the angle between the directions of propagation of the incident and scattered light. By means of the Mie theory, information concerning particle size may be obtained by (1) observation of the transmitted light as a function of wavelength, (2) measurement of the intensity of the scattered light at a given wavelength, (3) determination of the color of the scattered light, and (4) determination of the polarization of the scattered light at a given wavelength.

(17) **Ultramicroscopes:**<sup>1</sup> Zsigmondy's effort to examine the Tyndall effect under a microscope led to the development of an important tool for colloid investigations: the ultramicroscope. With this instrument it is possible to perceive the light scattered by a single particle too small to give an image by transmitted light in even the most powerful microscope. According to Abbe's theory, a particle smaller than  $\lambda/2NA$ , where  $\lambda$  is the wavelength and  $NA$  is the numerical aperture of the optical system, cannot give an image and is therefore invisible in the microscope. For aqueous colloidal solutions ( $NA < 1.3$ ) and "white" light ( $\lambda = \text{ca. } 550 \mu\mu$ ), the limit is reached<sup>2</sup> at  $200 \mu\mu$ . Provided the intensities are adequate, a self-luminous particle, regardless of its smallness, gives rise in the microscope to a diffraction pattern, which is visible when viewed against a dark background. The pattern of an ultramicroscopic particle of any shape is a circle of light surrounded by rings of diminishing intensity. Its size depends only upon the optical characteristics of the observing microscope. An ultramicroscope is a modified microscope with which very small particles may be rendered effectively self-luminous by indirect illumination in order that their diffraction patterns may be examined microscopically.

Several appliances for such dark-field illumination were designed by early English microscopists,<sup>3</sup> but received little attention. Special arrangements were invented almost simultaneously by Siedentopf and Zsigmondy<sup>4</sup> and by Cotton and Mouton<sup>5</sup> for the examination of colloidal solutions. In the former,

<sup>1</sup> Gage, *The Microscope* (14th ed., Ithaca: Comstock Publ. Co., 1925); Schirmann, *Ultramicroscopie in Abderhalden, Handb. biol. Arbeitsmethoden* (Berlin: Urban and Schwarzenberg, 1926), Part II, Sec. I.

<sup>2</sup> The resolving power may be about doubled by microinterferometric methods, according to Gerhardt, *Z. Physik*, 35, 697, 718 (1926); 44, 397 (1927); *Fortschr. Chem., Physik, physik. Chem.*, 20B, 1 (1928).

<sup>3</sup> For example, Wenham, *Trans. Microscop. Soc.*, 3, 83 (1850).

<sup>4</sup> Zsigmondy, *Ann. Physik*, 10, 1 (1903); *Zur Erkenntnis der Kolloide* (Jena: Fischer, 1905); translated by Alexander, *Colloids and the Ultramicroscope* (New York: John Wiley & Sons, Inc., 1909).

<sup>5</sup> Cotton and Mouton, *Compt. rend.*, 136, 1657 (1903); *Les ultramicroscopes* (Paris: Masson, 1906). Their arrangement is practically identical with that of Dubern (1888), according to Raman, *Phil. Mag.*, 17, 495 (1909).



which is the much used "slit-ultramicroscope," a reduced image of a highly illuminated adjustable slit is projected by means of a microscope objective *I* (Fig. 12) into the specimen *C* at right angles to the axis of the observing microscope *O*.

The slit and condenser types of ultramicroscopes each have certain advantages. The former is preferable for the rapid examination of fluid systems, particularly if the influence of the chamber walls is to be avoided. The latter

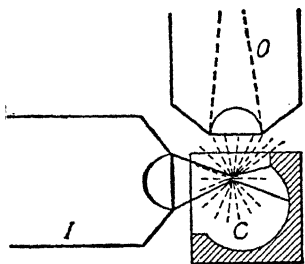


FIG. 12. Slit-Ultramicroscope with Orthogonal Illumination.

must be used on thin films and is better adapted to photomicrography.<sup>6</sup> In any case considerable care must be exercised in interpreting ultramicroscopic observations, particularly by distinguishing between particles of the colloid supposed to be present and particles of extraneous matter that are almost always present.

Since the intensity of scattered light from a rod- or disc-shaped particle is a maximum with the larger dimensions parallel to the electric vector of the incident beam, the Brownian motion of such particles causes them to twinkle or scintillate when they are suitably illuminated along one axis and examined in an ultramicroscope.<sup>7</sup> If the elongated particles are at rest, as in a gel, their visibility may be much changed by appropriate adjustment of the direction of illumination.<sup>8</sup>

The ultramicroscope played an important part in putting colloid science on a quantitative basis. Much of the experimental work on the molecular kinetic behavior of colloidal solutions would not have been possible without this instrument. The first reliable estimates of particle size in colloidal solutions were made by dividing the analytically determined mass of dispersed material per unit volume by the average number of particles in the same volume as determined by counting in the ultramicroscope.

(18) **Electron Microscope:**<sup>1</sup> The operation of the electron microscope depends upon the fact that electron beams are equivalent to light in the sense

<sup>6</sup> Dark-field photographs: Siedentopf, *Z. wiss. Mikroskop.*, 26, 391 (1909); Nordlund, *Z. physik. Chem.*, 87, 40 (1914); Darke, McBain, and Salmon, *Proc. Roy. Soc.*, A98, 395 (1921); Bachmann, *Z. anorg. Chem.*, 73, 125 (1912); von Weimarn, *Jellies and Gelatinous Precipitates*, 1928, and other publications. Motion pictures have been made by Eddy and Eddy, *J. Ind. Eng. Chem.*, 13, 1016 (1921); Hauser, *ibid.*, 18, 1146 (1926); Wightman and Trivelli, *ibid.*, 17, 164 (1925); Kraemer, *Second Colloid Symposium* (1924), p. 57.

<sup>7</sup> (a) Amann, *Kolloid-Z.*, 7, 70 (1910); 8, 11 (1911); (b) Siedentopf, *Z. wiss. Mikros.*, 29, 1 (1912); (c) Diesselhorst, Freundlich, and Leonhardt, *Elster-Geitel Festschrift*, 453 (1915); (d) Diesselhorst and Freundlich, *Physik. Z.*, 17, 117 (1916); (e) Freundlich, *Z. Elektrochem.*, 22, 27 (1916); (f) *Colloid and Capillary Chemistry* (1926), p. 403; (g) Kruyt, *Kolloid-Z.*, 19, 161 (1916); (h) Szegvari, *Physik. Z.*, 24, 91 (1923); (i) *ibid.*, 21, 348 (1924); (j) *Z. physik. Chem.*, 112, 277, 295 (1924).

<sup>8</sup> Szegvari, *loc. cit.*

<sup>1</sup> Zworykin, Morton, Ramberg, Hillier, and Vance, *Electron Optics and the Electron Microscope* (New York: John Wiley and Sons, Inc., 1945); Burton and Kohl, *The Electron Microscope*

that they can be bent by suitable magnetic or electrostatic fields, just as lenses bend light beams. The wavelength  $\lambda$  of the electron beam is given by the de Broglie relation  $\lambda = h/mv$ , where  $h$  is the Planck constant,  $m$  is the electron mass, and  $v$  is its velocity. In terms of the accelerating potential  $V$  expressed in volts,

$$\lambda = \frac{12.3}{V^{1/2}} \text{ \AA} \quad (18.1)$$

In the standard commercial instruments an accelerating potential of about 50,000 volts is used so that the electron beam has an effective wavelength of 0.05 Å. Actually, the smallest practical distance which is resolved at present is of the order of 30 Å, and a magnification power of 20,000 is readily attainable. Thus, it is possible to study directly particles in the colloidal size range.

The sample itself must be held on a cellulose nitrate membrane which is supported by a grid. The thickness of the sample on the membrane is rather critical; if it is too thin the electrons will not be sufficiently scattered to give good contrast, but if it is too thick the electrons will be stopped. The sample must be dry and capable of maintaining its character in a high vacuum. Various techniques have been developed which greatly enhance the value of the diagram which is obtained. Among them may be mentioned shadow-casting,<sup>2</sup> and heavy metal stains for biological specimens.<sup>3</sup>

The electron microscope is a very important tool in colloid chemistry because it permits the visualization of particles throughout the domain of colloidal dimensions. It provides one of two general methods, the other being sedimentation analysis, for studying the distribution of size in a fine powder or in such typical inorganic colloids as adsorbents, pigments, fillers and catalysts. If the shape of the particles is known, the specific surface area may be computed from the size distribution and compared with that obtained by using the adsorption techniques, e.g., titration with dyes, multimolecular adsorption, and surface energy (see p. 604).

**(19) Induced Double Refraction:**<sup>1</sup> External vectorial forces give to rise optical anisotropy in other properties than the Tyndall effect. The differences in Tyndall effect in different directions may be made macroscopically evident by giving the nonspherical particles a common orientation by means of external agencies that exercise a directive force upon the particles. Such agencies are shear, i.e., mechanical, or electric or magnetic fields. The effects of shear are quite simply illustrated by the silky streaks, or "schlieren," induced by stirring a dispersion of nonspherical particles. The particles become oriented by the velocity gradients with the longer dimensions in stream planes of constant velocity; depending upon the direction of the eddy currents at different points

(New York: Reinhold Publishing Co., 1942); R. W. G. Wyckoff, *Electron Microscopy* (New York: Interscience Publishers, 1949).

<sup>2</sup> Williams and Wyckoff, *J. Appl. Physics*, **15**, 712 (1944).

<sup>3</sup> Mudd and Anderson, *J. Expl. Med.*, **76**, 103 (1942).

<sup>1</sup> Edsall, *Advances in Colloid Science* (New York: Interscience Publishers, 1942), p. 269.

with respect to the illumination and the position of the observer, variations in the intensity of the Tyndall effect marking out the topography of the eddy currents produce the characteristic silky appearance.

Of special interest for the question of physical structure is the double refraction and dichroism that appear in certain colloidal solutions when in a magnetic<sup>2</sup> or electric field,<sup>3</sup> or when flowing nonturbulently.<sup>4</sup> According to Björnsthål a magnetic field produces positive double refraction in sols of gold ( $r = 6$  to 100  $m\mu$  by nuclear method), Biltz's ferric oxide, Schultze's antimony trisulfide, vanadium pentoxide, gelatin, and silver and platinum (by hydrazine reduction). No double refraction appears in very fine grained dispersions, as of Faraday gold, electropulverized metals (except when ferromagnetic), and precipitated sulfur. Mechanically pulverized sulfur sols, coarse Congo red, and Gutbier silver sols give negative double refraction. Streaming double refraction with a negative sign is shown by dispersions of Carey Lea silver and gold (nuclear), and with a positive sign by Graham's ferric oxide, Gutbier's silver ( $AgO?$ ), collodion, agar, gelatin, silicic acid, sodium oleate, and several oils. Zocher has described the streaming double refraction of sols of vanadium pentoxide, ferric oxide, tungstic acid, silver cyanate, clay, bentonite, soaps, benzopurpurin, benzo-brown, aniline blue, alizarin, sodium alizarinsulfonate, anthracene, cerasineorange, *p*-azoxyphenetole, *p*-azoxyanisole, and primuline.

Although induced double refraction is certainly due, in most cases, to the orientation of nonspherical particles, the detailed interpretation of the effects may be rather involved. A distinction must be made between a double refraction caused by the orientation of anisotropic particles (intrinsic double refraction) and a double refraction due to the orientation of isotropic particles in an isotropic medium of different refractive index (rod double refraction). The former may be positive or negative, the latter is always positive.<sup>5</sup> Both effects may occur simultaneously. In the case of the vanadium pentoxide sols, which have been most carefully investigated, and probably in most cases of pronounced effects, the induced double refraction is largely due to intrinsic double refraction of the particle.<sup>6</sup> The magnitude and even the sign of the effects need not be the same when different orienting agencies are used. For example, the double refraction of a gold sol was positive in a magnetic field and negative

<sup>2</sup> Called the Majorana effect and investigated by (a) Majorana, *Rendi. Accad. Lincei*, 11, 536, 539 (1902); 12, 90, 139 (1902); (b) Schmauss, *Ann. Physik*, 12, 186 (1903), found an appreciable relaxation time for the effect; (c) Cotton and Mouton, *Ann. chim. Phys.*, 11, 145, 289 (1907); (d) Björnsthål, *Phil. Mag.*, 42, 352 (1921); *Diss.*, Upsala, 1924.

<sup>3</sup> Björnsthål, *Phil. Mag.*, 2, 701 (1926).

<sup>4</sup> Kundt, *Ann. Physik*, 13, 110 (1881); deMetz, *ibid.*, 35, 497 (1888); *Compt. rend.*, 136, 604 (1903); Unlauf, *Ann. Physik*, 45, 304 (1892); Diesselhorst and Freundlich, *Physik. Z.*, 16, 419 (1915); 17, 117 (1916); Zocher, *Z. physik. Chem.*, 98, 293 (1921); Freundlich, Schuster, and Zocher, *ibid.*, 105, 119 (1923); Freundlich, Stapelfeldt, and Zocher, *ibid.*, 114, 161, 190 (1925); Arcaay and Etienne, *Compt. rend.*, 185, 700 (1927); ref. 2, (c) and (d).

<sup>5</sup> The theory of this effect has been dealt with by Wiener, *Abhandl. Sachs. Akad. Wissen., Leipzig*, 32, 575 (1912), and by Havelock, *Proc. Roy. Soc.*, A77, 170 (1906); 80, 28 (1908).

<sup>6</sup> Ref. 4, Freundlich, *et al*

when streaming.<sup>7</sup> Such variations in behavior can arise because the geometric (shape), optic, magnetic and electric axes of particles need not coincide. Inasmuch as the orientation due to flow depends directly on particle shape, streaming double refraction usually provides a more reliable indication of the shape than electric or magnetic double refraction.

A significant feature deserving investigation is the angle between the direction of shear and the optical axis of the oriented assemblage of particles. In the coarser dispersions, the angle is zero; in solids and jellies it is 45°; but in sols of soaps, gelatin, collodion, and even vanadium pentoxide, this angle is between 0 and 45°.<sup>8</sup> The particles in the sols mentioned seem to be united in some way, forming a more or less tenuous elastic structure that undergoes deformation as well as orientation. The effect is probably closely related to the phenomena to be mentioned in the next paragraph and to diffusion anomalies.

In certain concentrated sols, e.g., aged vanadium pentoxide, aged ferric oxide, benzopurpurin, etc., Zocher<sup>9</sup> has observed that nonspherical particles may spontaneously unite without external directing forces into loose anisotropic swarms; they can be dispersed by gentle stirring but then reappear. These systems belong between the crystalline and amorphous states to an intermediate state of partial order, which Friedel<sup>10</sup> designates as mesomorphic, and which includes the "liquid crystals." Since the swarms are more or less fluid, in some cases even displaying an internal Brownian motion, their occurrence reveals binding forces of considerable range between the constituent particles. These forces are probably identical in nature<sup>11</sup> with those which are responsible for gel formation, the special properties of pastes, thixotropic effects, and viscosity anomalies.

(20) **X-ray Analysis of Inorganic Colloids:**<sup>1</sup> The services rendered by X-rays have taken several forms: (1) the identification of crystal structure and therefore of chemical constitution, (2) the estimation of particle size and shape, and (3) the determination of the spatial relations between particles. An advantage, unique to X-ray analysis, lies in the fact that the information obtained refers to the smallest unit or primary particle of the dispersed material. Recent applications of X-rays have been made to the investigation of solutions of detergents (p. 670) and the structure of proteins (p. 652). The following investigations may also be mentioned.

(a) After a considerable period of uncertainty, and even differences in opinion, as to whether colloidal particles are amorphous or crystalline, X-ray

<sup>7</sup> Björnsthåhl, *loc. cit.*

<sup>8</sup> Freundlich, Stapelfeldt, and Zocher, *loc. cit.*; Freundlich, Neukircher, and Zocher, *Kolloid-Z.*, **38**, 43, 48 (1926); Björnsthåhl, *loc. cit.*

<sup>9</sup> Zocher, *Z. anorg. Chem.*, **147**, 91 (1925); Zocher and Jacobson, *Kolloid-Z.*, **41**, 220 (1927); *Kolloidchem. Beih.*, **28**, 167 (1929). In the last paper, these sols are called "tactosols." Von Weimarn, *Kolloid-Z.*, **44**, 279 (1928).

<sup>10</sup> Friedel, in Alexander, *Colloidal Chemistry*, Vol. I, chap. 3; *Ann. phys.*, **18**, 274 (1922).

<sup>11</sup> Freundlich, *Ber.*, **61**, 2219 (1928).

<sup>1</sup> General reference: Clark, *Applied X-rays* (3d ed.; New York: McGraw-Hill Book Co., Inc., 1940).

methods forced a compromise by showing that the bulk of the particle may be either undeniably crystalline or as amorphous as a simple liquid, with intermediate conditions also possible. For instance, colloidal particles of gold, silver, insoluble halides, and metallic oxides or hydroxides, give the same diffraction patterns as the corresponding materials in bulk.<sup>2</sup> "Copper" sols by the Bredig method are largely cupric oxide;<sup>3</sup> the residue from "ferric oxide" sols (by Graham's method) may contain crystalline basic ferric chloride or goethite  $[\text{FeO}(\text{OH})]$ ; <sup>4</sup> and transparent barium sulfate gels <sup>5</sup> contain normal crystals. In contrast to these, silica, stannic oxide, ferric oxide, alumina, sulfur, and beryllium hydroxide can be prepared having no more crystallinity than a liquid. A gradual development of crystalline particles may occur in some of these cases upon aging or with suitable treatment, such as hot digestion with water or electrolyte solutions.

(b) The estimation of particle size and shape depends upon modifications of the distribution of intensity in the diffraction patterns. For particle sizes about  $10^{-2}$  mm, the lines in a powder-diffraction pattern are broken or spotted; as the size falls below  $10^{-4}$  mm, the lines broaden and become increasingly diffuse.

Qualitative comparisons of line breadth for the insoluble "hydrous oxides" have yielded considerable information concerning the colloidal state of these materials.<sup>6</sup> Sols and gels of the hydrated oxides of the quadrivalent elements, when freshly prepared at room temperatures, are practically amorphous (in the X-ray sense); that is, crystalline particles, if present, are but little larger than atomic dimensions. Upon aging, larger and larger crystalline particles of the anhydrous oxides appear. Gelatinous precipitates of ferric and aluminum hydroxides are amorphous when formed from cold concentrated solutions; crystals of hydroxides, viz., hydrargillite  $[\text{Al}(\text{OH})_3]$ , böhmite  $[\text{AlO}(\text{OH})]$ , goethite  $[\text{FeO}(\text{OH})]$ , or lepidocrocite  $[\text{FeO}(\text{OH})]$ , appear and gradually increase in size during aging or hot digestion. Sols of these materials as well as of the hydroxides of beryllium, magnesium, and zinc, the halides of silver, and the sulfides of the heavy metals probably as a rule contain crystals. Weiser and Milligan <sup>7</sup> have investigated hydrous oxides with simultaneous dehydration studies and X-ray diffraction analysis.

Scherrer <sup>8</sup> calculated theoretically that the angular breadth  $B$  of a diffrac-

<sup>2</sup> Scherrer, *Nachr. Konigl. Ges. Wiss. Göttingen*, 98 (1918); appendix in Zsigmondy, *Kolloidchemie* (3d ed.; 1920); Böhm, *Kolloid-Z.*, 42, 276 (1927), gives a review of earlier work.

<sup>3</sup> Freundlich and Kroch, *Z. physik. Chem.*, 124, 158 (1926).

<sup>4</sup> Böhm, *loc cit.*

<sup>5</sup> von Weimarn and Hagiwara, *Kolloidchem. Beih.*, 23, 400 (1927).

<sup>6</sup> Fricke and co-workers, general summary, *Kolloid-Z.*, 49, 229 (1929); Böhm, and co-workers, *ibid.*, 42, 276 (1927). A report of a symposium on the subject appeared in *Z. anorg. Chem.*, 42, 595, 885 (1929).

<sup>7</sup> Weiser and Milligan, *J. Phys. Chem.*, 36, 3010 (1932); 38, 1175 (1934); *Chem. Rev.*, 25, 1 (1939); *J. Phys. Chem.*, 40, 1, 1095 (1936).

<sup>8</sup> Scherrer, *loc. cit.* A more general theoretical analysis has been given by von Laue, *Z. Krist.*, 64, 115 (1926). It is the basis for a method for particle-size determination (Brill,

tion line, measured between points of half the maximum intensity, is related to the diffraction angle  $\theta$ , the wavelength  $\lambda$ , and the thickness  $d$  of a cubic crystal by the equation

$$B = 2 \sqrt{\frac{\ln 2}{\pi}} \frac{\lambda}{d \cos \theta/2} + b \quad (20.1)$$

where  $b$  is an empirical instrument constant. For a particular Faraday gold sol, Equation (20.1) gave a value of  $1.9 \text{ m}\mu$  for  $d$ , whereas Zsigmondy estimated it to be  $1.6 \text{ m}\mu$  from the osmotic pressure. The X-ray method has been applied to the metal "blacks" of the platinum family in investigations of particle size and catalytic activity.<sup>9</sup> The estimation of the dimensions of the crystallites in native ramie fiber<sup>10</sup> illustrates a more refined application of the method. The crystallite appears to be a parallelepiped having average dimensions of  $50 \times 50 \times$  at least  $500 \text{ \AA}$ , and containing 6,000 to 12,000 glucose residues. The average crystallite in racked rubber<sup>11</sup> is estimated to be 300 to  $600 \text{ \AA}$  long and 100 to  $200 \text{ \AA}$  thick, on the assumption that the breadth of the diffraction lines is not due to imperfect lattices.

#### MECHANICAL PROPERTIES OF COLLOIDAL SOLUTIONS

(21) **Viscosity:** All fluids display internal friction. Expressed as the viscosity coefficient of a pure liquid, it is quantitatively defined by Newton's law as the ratio of the shearing stress  $\tau$ , per sq cm to the velocity gradient  $dv/dx$  which is produced, i.e.,

$$\eta = \tau / (dv/dx) \quad (21.1)$$

As long as turbulence does not occur,  $\eta$  is a constant for simple liquids. When the Reynolds number exceeds 2,000, however, streamline flow breaks down into turbulent flow, and the velocity gradient cannot be accurately described; the viscosity is then no longer the determining factor in controlling the rate of flow. Thus, for many colloidal systems  $\tau/(dv/dx)$  is not a constant and the rheological behavior is said to be "non-Newtonian." The velocity gradient as a function of shearing stress for (a) a Newtonian liquid, (curve C), and (b) non-Newtonian liquids, (curves A, B, and D) is shown in Fig. 13.

For simple "Newtonian" liquids the viscosity is commonly measured by studies of flow through capillary tubes, flow between concentric cylinders, or

*Z. Krist.*, **68**, 387 (1928); Brill and Pelzer, *ibid.*, **72**, 398 [1929], *Z. tech. Physik*, **10**, 663 [1929]), which is free from the difficulty of estimating line breadths by photographic photometry; the employment of a hollow-cylinder form for the specimen results in the splitting of each interference into a doublet, from the separation of which particle size can be calculated. Patterson, *Z. Krist.*, **66**, 637 (1928), and Mark, *Trans. Faraday Soc.*, **25**, 387 (1929), emphasize the theoretical and experimental uncertainties and difficulties in estimating particle size by X-ray methods.

<sup>9</sup> Levi and Haardt, *Atti. Accad. Lincei*, **3**, 91, 215 (1926).

<sup>10</sup> Hengstenberg and Mark, *Z. Krist.*, **69**, 271 (1929); *Z. physik. Chem.*, **2B**, 115 (1929).

<sup>11</sup> Hengstenberg and Mark, *loc cit.*

rate of fall of a sphere or other object. For any and each method to be absolute, Newton's law must be integrated with suitable boundary conditions to obtain the relationship between coefficient of viscosity and the observable quantities.

In certain cases, such as very concentrated solutions of high molecular weight substances or concentrated colloidal suspensions, the viscosity may be

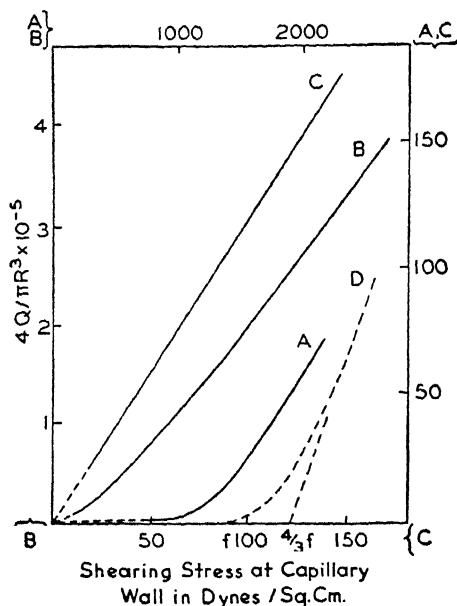


Fig. 13. Typical Rate of Shear vs. Maximum Shearing Stress Curves for Dispersed Systems Flowing through Capillary Viscometers.

- A. 25 volume per cent zinc oxide in linseed oil; apparent relative viscosity falls from 1335 to 60 with increasing shearing stress.
- B. 0.2 volume per cent dynamite nitrocellulose in acetone; apparent relative viscosity varies between 6.3 and 2.2.
- C. 9 volume per cent titanox in mixture of linseed oil and petroleum hydrocarbon; relative viscosity is constant and equal to 2.28.
- D. Ideal plastic flow according to the Schwedoff-Bingham-Buckingham theory. The straight line cutting the stress axis at  $\frac{4}{3}f$  is the asymptote to D at high stresses.

not only a function of the shearing stress but also of the previous history of motion within the liquid. In a thixotropic system the viscosity decreases with the length of time the liquid has been in motion. Sol-gel transformations in such systems depend upon the breaking up and reformation of particle arrangements within the liquid.

In general, the results obtained by viscosity measurements on solutions containing macromolecules have been interpreted either in terms of a shape factor or a solvation factor for the solute. The idea of an elongated molecule

has found considerable favor in protein chemistry.<sup>1</sup> In another large class of high molecular weight substances, the elastomers, it is believed that the molecular chain winds at random through the solvent molecules to give the equivalent of small sections of swollen gel within the system. In the case of such systems extremely high axial ratios are obtained if the high intrinsic viscosities are explained as being caused by deviations from spherical shape. Such ratios are of little value.

**(22) Newtonian Fluids:** The first rigorous hydrodynamic analysis of the viscosity of colloidal solutions is that of Einstein.<sup>1</sup> For the ideal case of a suspension of rigid spheres of uniform size, in which the radius  $r$  of the particles is small with respect to the mean distance  $a$  between them, i.e.,  $r \ll a$ , and with respect to the smallest dimension of the shearing liquid, e.g.,  $r \ll R$ , where  $R$  is the radius of a capillary viscometer, but is large with respect to the thickness of the liquid layer adhering to the spheres, Einstein showed that the viscosity  $\eta$  of the suspension should be given by the equation

$$\frac{\eta}{\eta_0} = 1 + 2.5\phi = 1 + 2.5 cv \quad (22.1)$$

where  $\eta_0$  is the viscosity of the medium,  $\phi$  is the fraction of the volume occupied by the dispersed spheres,  $c$  is the concentration in g/ml, and  $v$  is the partial specific volume of the dispersed phase. Equation (22.1) represents the limiting case for infinitely small changes in viscosity; for moderate changes in viscosity it should and does give too small values for the relative viscosity.

Further, from Equation (22.1), it appears that the relative viscosity of a very dilute suspension is dependent only on the volume concentration, but is independent of particle size, temperature or viscosity of the solvent. There is always a difficulty in any experimental test of the equation because the true volume concentration of a colloid solution is unknown. If volume concentration is calculated from the density of the undissolved solute or from its partial specific volume and if solvation is ignored, some colloids and macromolecules give agreement to within 25 per cent. The equation is now usually accepted as being valid for spherical particles and any discrepancy is assumed to be due to increased volume concentration from solvation, or to nonspherical particle shape which also increases the viscosity above that given by Einstein's equation.

In general macromolecules deviate from spherical form and the viscosity at a given concentration of their solutions is many times greater than it would be for dissolved spheres of corresponding phase volume. It is now a universally accepted principle of colloid chemistry that long molecules and high viscosity go together. To describe the effect of a dissolved or suspended material on the viscosity, a quantity called the "intrinsic viscosity"  $[\eta]$  is now widely used.

<sup>1</sup> Svedberg and Pedersen, *The Ultracentrifuge* (1940); Oncley, *Ann. N. Y. Acad. Sci.*, **41**, 121 (1941).

<sup>1</sup> Einstein, *Ann. Physik*, **19**, 289 (1906); **34**, 591 (1911); von Smoluchowski, *Kolloid-Z.*, **18**, 190 (1916).



It is defined as

$$[\eta] = \lim_{c \rightarrow 0} \left[ \frac{\eta_r - 1}{c} \right] \quad (22.2)$$

where  $\eta_r = \eta/\eta_0$  is the "relative viscosity." The choice of unit of concentration must be observed with care. As has been mentioned, the volume concentration is actually unknown, and so most investigators use grams solute per 100 ml solution. Then

$$[\eta]_v = \frac{[\eta]}{\bar{V}} = \lim_{c \rightarrow 0} \left[ \frac{\eta_r - 1}{c \bar{V}} \right] \quad (22.3)$$

where  $c$  is the concentration in g/100 ml and  $\bar{V}$  is the partial specific volume of solute. For unsolvated spherical particles or molecules  $[\eta]_v = 0.025$ .

Experiment shows that the linear relationship between  $\eta_r - 1$  and concentration required by Equation (22.1) is restricted to a very narrow range. For higher concentrations and in situations where deviations from spherical form are known, the basic equation has been modified by many workers. For one thing it became necessary in the case of rod-shaped or laminar particles to distinguish between coarse and fine particle suspensions, because with the latter consideration must be given to the Brownian motion. A number of these equations for the "specific viscosity," i.e.,  $\eta_r - 1$ , of solutions are summarized in Table VIII.<sup>2</sup>

The viscosity of solutions of linear polymeric molecules is a continuous function of the length of the molecule, thus giving a kind of proportionality between viscosity and molecular weight. Such proportionality is expressed by the so-called Staudinger law,

$$\eta_{sp} = K_m M c \quad (22.4)$$

where  $K_m$  is a constant characteristic of each homologous polymeric system and solvent,  $\eta_{sp}$  is the specific viscosity,  $c$  is the concentration expressed in base moles per liter, and  $M$  is a weight average molecular weight. Actually this expression often fails when tested experimentally, and it seems preferable to write

$$[\eta] = K_m M^a \quad (22.5)$$

where  $a$  is a constant. When  $a$  is 1, we have the Staudinger case, but frequently, as in the case of flexible chain-like molecules,  $a$  has a value near 0.70. When  $a \neq 1$ , the molecular weight will not be of the weight-average type, but will be what may be termed "viscosity average" molecular weight. Actually, Debye<sup>3</sup> has given a detailed picture of the motion of the polymer molecule and its parts, and makes it evident why the rule is effective. Kirkwood and Risman<sup>4</sup> have developed a theory of the intrinsic viscosity and translational diffu-

<sup>2</sup> Adapted from Mark and Tobolsky, *Physical Chemistry of High Polymeric Systems*, 2d ed. (New York: Interscience Publishers, 1950).

<sup>3</sup> Debye, *J. Chem. Phys.*, **14**, 636 (1946).

<sup>4</sup> *J. Chem. Phys.*, **16**, 565 (1948).

TABLE VIII  
EXPRESSIONS FOR THE SPECIFIC VISCOSITY OF SOLUTIONS AND SUSPENSIONS

Type of suspension or solution		At extreme dilution			At moderate concentrations
		Without Brownian movement	With complete Brownian movement		Without Brownian movement
Rigid spheres		Einstein, Simha $2.5\ c$			Gold, Guth, and Simha $2.5\ c + 14.1\ c^2$
Liquid (soft) spheres		Taylor $r \times c$ ; with $r$ varying from 2.5 to 1			—
Rigid rod-like particles	Minimum value	Jeffery $2.0\ c$	Guth, Huggins, Jeffery $2.0\ c$	Simha	—
	Maximum value	Jeffery $\left[\frac{f}{2\ln 2f-3}+2\right]c$ Eisenschitz $\frac{1.15f}{11\ln 2f}c$	Huggins, Kuhn $(2.5+f^2/16)c$ Eisenschitz $\frac{f^2}{15\ln 2f-\frac{45}{2}}\cdot c$	$\left[\frac{f^2}{15(\ln 2f-\frac{3}{2})}+\frac{f^2}{5(\ln 2f-\frac{1}{2})}+\frac{14}{15}\right]\cdot c$	Gold and Guth $\left[\frac{f}{2\ln 2f-3}+2\right]c$ $+\frac{kf^3}{(2\ln 2f-3)^2}c^2$
Rigid disks	Minimum value	Jeffery $2.06\ c$	Guth $\frac{5}{12}\frac{f}{\tan^{-1}f}\cdot c$	$\frac{16}{15}\frac{f}{\tan^{-1}f}\cdot c$	—
	Maximum value	Jeffery $\frac{4f}{3\tan^{-1}f}c$	Guth, Jeffery $\left[\frac{4f}{3\tan^{-1}f}\right]^2\cdot c$		

sion of flexible macromolecules on the basis of the random coil model with hindered rotation. The significance of viscosity measurements on dilute solutions of high polymers has been considered in detail by Ewart.<sup>5</sup>

As noted, the results obtained by viscosity measurements on solutions of proteins have been often interpreted in terms of a shape factor for the molecules, but, as in the case of sedimentation and diffusion rate studies, the effect of solvation cannot be accurately computed. Various workers<sup>6</sup> have compared

<sup>5</sup> Ewart, *Advances in Colloid Science*, Vol. II (New York: Interscience Publishers, 1946), p. 197.

<sup>6</sup> See, for example, Polson, *Kolloid-Z.*, 88, 51 (1939); Mehl, Oncley, and Simha, *Science*,

the shape factors derived from the two types of measurement—viscosity and classical physical—and in general the agreement is quite good.

It is in the case of solutions of organic high polymers that the viscosity measurements have been most widely used in recent years. They have a certain practicability, especially as the sedimentation and diffusion methods have hardly been extended to these substances. It has been concluded that this type of molecule in solution has the form of a highly-kinked chain which in average configuration occupies a roughly spherical volume much larger than the true molecular volume. The excess in apparent volume is due to solvent molecules which have been mechanically trapped rather than actually bound by any valence forces. The phase volume  $\phi$  then depends on the number of atoms in the polymer chain, the length of the primary valence bond between atoms, the angles between bonds and the degree of freedom of rotation about these bonds. It decreases with increase in temperature because the tendency to randomness of rotational position is thereby increased.

(23) **Non-Newtonian Flow:** Another feature which complicates the interpretation of internal friction in colloidal systems, but which probably will contribute significant information concerning their physical structure, is their failure to behave in accordance with Equation (21.1). A given colloidal solution may appear to have different viscosities when measurements are made with different instruments, or even when the same instrument is used at different shearing stresses.<sup>1</sup> In practically all such cases, the viscosity coefficient, as calculated in the usual way, decreases with increase in the rate of shear. The value so obtained is often qualified as an "apparent viscosity" to distinguish it from the constant characterizing the internal friction of a simple liquid, and the dispersions are said to be "plastic solids"<sup>2</sup> or "elastic liquids" possessing "structural viscosity."<sup>3</sup> This anomalous behavior is displayed most markedly by dispersions that depart widely from Einstein's equation, although not by all such cases. Figure 13 shows some typical results, obtained with capillary viscometers. Two types of curves may be distinguished, although there is no clear-cut demarcation between them.

One form (curve A) is characterized by a very low rate of flow until a certain stress is exceeded, beyond which the rate increases rapidly. These systems

92, 132 (1940); Lauffer, *Chem. Rev.*, 31, 561 (1942); Oncley, *J. Phys. Colloid Chem.*, 51, 184 (1947).

<sup>1</sup> This property was already studied by Schwedoff, *J. phys.*, 9, 34 (1890) and Garrett, *Phil. Mag.*, 6, 374 (1903). Later work, especially by Hatschek *Kolloid-Z.*, 12, 238, 13, 88 (1913); *The Viscosity of Liquids* (London: George Bell & Sons, Ltd., 1928); Hess, *Kolloid-Z.*, 27, 1, 154 (1920); and Bingham, *Bur. Standards Sci. Paper*, No. 278 (1916); *Fluidity and Plasticity* (New York: McGraw-Hill Book Co., Inc., 1922), led to a more general recognition of the importance of the phenomenon. Rapid and convenient capillary methods for measuring the property have been described by Bingham and Murray, *Proc. Am. Soc. Testing Materials*, 23, II, 655 (1923) and by Ostwald and Auerbach, *Kolloid-Z.*, 38, 261 (1926); 41, 56 (1927).

<sup>2</sup> Bingham, *op. cit.*

<sup>3</sup> Freundlich, *Colloid and Capillary Chemistry* (3d ed.; New York: E. P. Dutton & Sons, Inc., 1926); Ostwald, *Kolloid-Z.*, 11, 230 (1912).

often show an appreciable rigidity or form-elasticity<sup>4</sup> and to this extent resemble gels. Schwedoff<sup>5</sup> suggested that such dispersions have a yield point, above which continuous shear can take place with a linear relationship between rate of shear and shearing stress; quantitatively, the internal friction should then be characterized by the equation

$$\eta' = \frac{\tau - f}{dv/dx} \quad (23.1)$$

instead of the simpler Newton Equation (21.1). In this expression  $\eta'$  and  $f$  are constants, the former being equal to the limiting value of the apparent viscosity at high rates of shear and  $f$  representing the minimum stress that produced continuous shear. This assumption forms the foundation of Bingham's theory of "plastic" flow and has served as the starting point for numerous investigations.<sup>6</sup> The practical, i.e., integrated, equations have been worked out by Buckingham<sup>7</sup> (for capillary methods) and by Reiner and Rivlin<sup>8</sup> (for both capillary and concentric-cylinder methods). Curve *D*, corresponding to the equation

$$Q = \frac{\pi R^3 F}{4l\eta'} \left[ 1 - \frac{4}{3} \frac{f}{F} + \frac{1}{3} \left( \frac{f}{F} \right)^4 \right] \quad (23.2)$$

illustrates the relations predicted by this theory. The discrepancies between theory and observations are said to be due to slippage<sup>9</sup> at the instrument walls or seepage<sup>10</sup> of the dispersion medium. It has not been found possible in general to incorporate these explanations quantitatively into the theory so as to make it accord with observations without further *ad hoc* hypotheses.

One of the principal factors preventing the theoretical treatment of this type of curve is the badly defined character of the internal friction and mechanical properties of the dispersions.<sup>11</sup> The resistance which they offer to shear is often quite sensitive to mechanical working, the shear during a measurement

<sup>4</sup> Hess, *Pflüger's Arch. ges. Physiol.*, **162**, 187 (1915); Freundlich and Seifriz, *Z. physik. Chem.*, **104**, 233 (1923); Seifriz, *Third Colloid Symposium*, 1925, p. 285; Hatschek and Jane, *Kolloid-Z.*, **38**, 33, 39, 300 (1926); Freundlich and Rawitzer, *Kolloidchem. Beih.*, **25**, 231 (1927); Ostwald, Auerbach, and Feldmann, *Kolloid-Z.*, **43**, 155, 181 (1927); Blair and Crowther, *J. Phys. Chem.*, **33**, 321 (1929).

<sup>5</sup> *Loc. cit.*

<sup>6</sup> See summary by Herschel, in Alexander, *Colloid Chemistry*, Vol. I, chap. 45; Szegvari, *Z. physik. Chem.*, **108**, 175 (1924); Freundlich and Schalek, *ibid.*, **108**, 153 (1924); Freundlich, Stapelfeldt, and Zocher, *ibid.*, **114**, 190 (1925); Freundlich, Neukircher, and Zocher, *Kolloid-Z.*, **38**, 43, 48 (1926); Freundlich and Nitze, *ibid.*, **41**, 206 (1927).

<sup>7</sup> Buckingham, *Proc. Am. Soc. Testing Materials*, **21**, II, 1154 (1921).

<sup>8</sup> Reiner and Rivlin, *Kolloid-Z.*, **39**, 80 (1926); **43**, 1 (1927).

<sup>9</sup> As a matter of fact, slippage without shear except at the wall normally occurs at low stresses whenever the shear-stress curve has the form of *A* or the dispersion shows a detectable bulk-rigidity. Cf. Green, *Proc. Am. Soc. Testing Materials*, **20**, II, 451 (1920); Blair and Crowther, *loc. cit.*

<sup>10</sup> Bingham, *op. cit.*

<sup>11</sup> Hatschek and Jane, *Kolloid-Z.*, **38**, 33 (1926); Ostwald, *et al.*, *loc. cit.*; Biltz and Steiner, *Z. physik. Chem.*, **73**, 500 (1910).

reducing the internal friction and preventing duplication of the results. Upon standing undisturbed, the dispersion may more or less gradually regain its rigidity. This phenomenon of spontaneous repair of the broken structure has received the name "thixotropy"<sup>12</sup> and has been particularly studied by Freundlich and his associates.<sup>13</sup> On the whole, these various effects appear to be due to partial flocculation or gelation. These dispersions may be considered as fragile solids or very weak gels the structure of which is readily broken down. In reality, the use of the term viscosity is misleading because the resistance to shear of such dispersed systems is a complicated function of viscosity, rigidity, and elasticity, besides slippage or other wall effects. By preventing flocculation (cf. curve *C*) no anomalous viscosity behavior or thixotropy occurs.

Curve *B* represents the behavior of a group of dispersions which, there is some reason for believing, differ in kind, but perhaps will be found to differ only in degree from those just described. The extrapolations that appear most plausible pass through the origin with a slope definitely greater than zero, in agreement with the fact that no rigidity or elasticity is detectable in the dispersions. The maximum curvature seems to be at the origin. These dispersions are usually much less sensitive to mechanical working than those represented by curve *A*; the same rate of shear may repeatedly be observed at a given stress, within the usual range of experimental error. Whereas the non-Newtonian behavior of group *A* depends upon gelation or aggregation that produced bulk rigidity, the variable viscosity of group *B* probably is due to the presence of separated particles or aggregates that can be oriented, deformed, or deflocculated by shearing stresses, depending upon their shape and structure. In cases where loosely united aggregates are the cause of the anomalous viscosity, the dispersions are apt to show a reduced resistance to shear after flowing; moreover a suitable change in dispersion medium may eliminate the variable viscosity.<sup>14</sup>

The investigation of curves belonging to the *B*-group has emphasized the limitations of the theoretical treatment originally given to the *A*-group and has led to numerous efforts to find a more general formulation of the phenomena. A number of empirical flow-stress equations have been proposed, and several substitutes for Newton's viscous resistance law have been tried out, but with only limited success.<sup>15</sup> The simplest equation that corresponds qualitatively with observations and that has been worked out completely is due to Reiner.<sup>16</sup>

Following the earlier work of Schwedoff and of Bingham, others began the study of the non-Newtonian flow of macromolecular solutions, especially of nitrocellulose and of rubber, and Herschel and Bulkley<sup>17</sup> showed that such

<sup>12</sup> Péterfi, *Arch. Entwicklungsmech. Organ.*, 112, 660 (1927).

<sup>13</sup> Schalek and Szegvari, *Kolloid-Z.*, 32, 318, 33, 326 (1923); Freundlich, *Kolloid-Z.*, 46, 289 (1928). The phenomenon is often observed in various pastes of industrial importance, such as dyes, paint pigments, and similar fine powders when wetted with suitable liquids.

<sup>14</sup> Sheppard and Houck, *J. Rheology*, 1, 20 (1929).

<sup>15</sup> These equations have been compared and discussed by Hatschek, *op. cit.*

<sup>16</sup> *J. Rheology*, 1, 11 (1929).

<sup>17</sup> Herschel, *loc. cit.*

solutions exhibit no yield value and do not obey the Schwedoff-Bingham plasticity equation. The idea gradually became prevalent that such solutions are characterized by a definite viscosity at very low rates of shear and another and lower viscosity at very high rates of shear, with a smooth transition in between. It was Reiner<sup>18</sup> who developed the first mathematical theories based upon this new and basic idea. Ostwald<sup>19</sup> and his students have applied the term "structure viscosity" to such behavior, but a definite and final determination of the molecular or particle characteristics is extremely difficult because so many factors may be involved. An excellent monograph descriptive of the subject is that of Philippoff.<sup>20</sup>

(24) **Electroviscous Effect:** If the particles (or molecules, or ions) carry an electric charge, the numerical coefficient of Equation (22.1) is increased by a factor due to an electroviscous effect;<sup>1</sup> thus,

$$\frac{\eta}{\eta_0} = 1 + 2.5\phi \left[ 1 + \frac{1}{\kappa\eta_0} \left( \frac{D\zeta}{4\pi r} \right)^2 \right] \quad (24.1)$$

where  $D$ ,  $\kappa$ , and  $\eta_0$  are the dielectric constant, specific conductivity and viscosity of the medium, respectively, and  $\zeta$  is the electrokinetic potential (see p. 630), the electrical quantities being in electrostatic units. If  $\kappa$  is  $10^{-5}$  ohm<sup>-1</sup> cm<sup>-1</sup>  $r$  is 10 m $\mu$ ,  $D$  is 80, and  $\zeta$  is 0.025 volt, the specific viscosity  $(\eta - \eta_0)/\eta_0$  should be increased about 13 times by the electroviscous effect. This phenomenon has been investigated by Kruyt and his co-workers<sup>2</sup> in colloidal solutions of starch, agar, gelatin, gum arabic, casein, and arsenic trisulfide. Figure 14 illustrates the magnitude of the effect. Kruyt and Tendeloo have also estimated particle size by solving Equation (24.1), two at a time, for both  $\phi$  and  $r$  (assuming that they remain constant) when  $\eta$  and  $\zeta$  are caused to vary by additions of electrolytes. In the case of starch sol, the radius of the hydrated particle was calculated to be ca. 9 m $\mu$ , and the estimated water con-

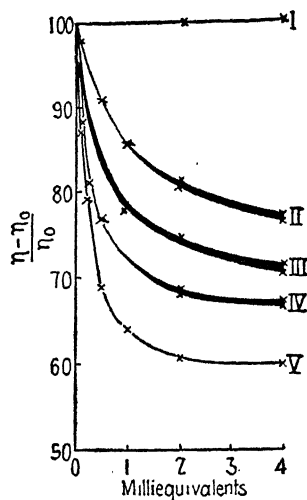


Fig. 14. Electroviscous Effect in 0.14 Percent Agar Sols at 50°C. as Revealed by the Effect of Added Substances upon the Relative Viscosity. Kruyt and de Jong, *Kolloidchem. Beih.*, 28, 1 (1928).

- I. Nonelectrolytes: urea, sucrose, and isoamyl alcohol.
- II. KCl, NaCl, LiCl, NH<sub>4</sub>Cl, KCNS, K<sub>2</sub>SO<sub>4</sub>, K<sub>4</sub>Fe(CN)<sub>6</sub>.
- III. BaCl<sub>2</sub>, SrCl<sub>2</sub>, MgSO<sub>4</sub>, CdSO<sub>4</sub>.
- IV. La(NO<sub>3</sub>)<sub>3</sub>, Co(NH<sub>4</sub>)<sub>6</sub>Cl<sub>3</sub>.
- V. Pt[C<sub>2</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub>]<sub>3</sub>(NO<sub>3</sub>)<sub>4</sub>.

<sup>18</sup> Reiner, *Kolloid-Z.*, 50, 199 (1930); *J. Rheol.*, 1, 14 (1929).

<sup>19</sup> Ostwald, *Kolloid-Z.*, 11, 230 (1912).

<sup>20</sup> *Viscosität der Kolloide* (Dresden: Steinkopf, 1942).

<sup>1</sup> von Smoluchowski, *Kolloid-Z.*, 18, 190 (1916).

<sup>2</sup> Kruyt, *Colloids* (New York: John Wiley & Sons, Inc., 1927); *Kolloidchem. Beih.*, 28, 1, 407 (1928-29); 29, 396, 413, 432, 436 (1929).

tent of the particle was over 91 per cent. In view of the uncertainties still existing with respect to the effective dielectric constant and the absolute magnitude of electrokinetic potentials, it is difficult to place the same confidence in these values of particle size as in those obtained with the more direct methods discussed earlier.

As an example of the existence of an electroviscous effect in a protein system, reference may be made to viscometric researches with gelatin to characterize it for clinical appraisal as a blood substitute. In many ways this is the most convenient and most sensitive method for the determination of the degree of degradation of the gelatin molecules.<sup>3</sup> Even so, it is fraught with difficulties because the intrinsic viscosity which is obtained for any given sample varies with the pH (and the ionic composition) of the system. It is only at the isoelectric point that a minimum and characteristic value will be obtained, one which will be related to the average molecular weight for such solutions.

## THE PHYSICAL CHEMISTRY OF INTERFACES

According to the state of aggregation of the phases in contact, interfaces may be classified as *mobile* or *immobile*. The former involve only fluid phases, and the latter involve one or more solid phases; thus,

### *Mobile Interfaces*

Liquid||Gas  
Liquid||Liquid

### *Immobile Interfaces*

Solid||Gas  
Solid||Liquid  
Solid||Solid

The energy relations of interfaces with solids are the same as those of liquids, except insofar as they are modified by the more specific structure of the surface of the solid. However, since the experimental methods for investigating mobile and immobile interfaces are quite different, they may appropriately be discussed separately.

## MOBILE INTERFACES<sup>1</sup>

(25) **The Energy of Surfaces:** The most obvious property of a mobile interface is its tendency to shrink to a minimum. Liquid drops suspended in a gas or in another liquid, and gas bubbles in liquid all assume a spherical form in the absence of extraneous influences such as gravity. The molecular interpretation of this tendency to contract is that the surface molecules are continually moving inwards more rapidly than others move outwards to take their places because in the surface molecules are subject to a strong inward attraction, perpendicular to the surface, as a result of the unbalance of the outward attraction by the vapor molecules and the inward attraction by the molecules in the

<sup>3</sup> Scatchard, Oncley, Williams, and Brown, *J. Am. Chem. Soc.*, **66**, 1980 (1944).

<sup>1</sup> General discussions of this topic are given by Adam, *The Physics and Chemistry of Surfaces* (3d ed.; New York: Oxford University Press, 1941), and Harkins, in Alexander, *Colloid Chemistry*, Vol. V, chap. I. See also this volume, p. 412 *et seq.*

liquid. The number of molecules in the surface is therefore continually diminishing, and the contraction of the surface continues until the maximum possible number of molecules are in the interior. On the other hand, work is required to extend the surface because molecules must be brought from the interior to the surface against inward attractive forces. Since a liquid surface contracts spontaneously and work must be done to extend the surface, there is free energy associated with the surface. Although surface free energy is the fundamental property of surfaces it is usually replaced, in solving problems, by its mathematical equivalent, viz., surface tension. This tension, which may be quantitatively defined as the contractile force in dynes operating in the plane of the interface and normal to a line in the interface 1 cm long, has the same dimensions and numerical magnitude as the surface free energy.

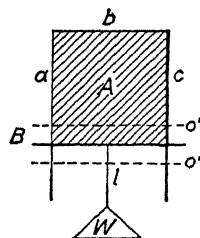


FIG. 15. Dupré's Model for Surface-Tension Relations.

The surface tension is different from the tension of an elastic surface film as may be illustrated by means of a model due to Dupré<sup>1</sup> (Fig. 15). A liquid film *A* is supported in air (or other fluid) *B*, between the fixed framework *abc* and the moveable barrier *l*. The tension of the two faces of the film pulling upward along *l* is just balanced by the force *W* directed downward. So far, the surface tension resembles the tension in a rubber sheet supported similarly. Differences become evident, however, upon changing the downward force *W*. For a very small decrease in *W*, a rubber membrane shrinks slightly, lifting *l* to a new position represented by *o'*, whereas the liquid film contracts until *l* is in contact with *b* and the film disappears. On the other hand for a very small increase in *W*, the rubber film stretches to the position *o''*, whereas the liquid film stretches indefinitely until it disappears by breaking. In other words, the tension in an elastic membrane may have various values depending upon its extension, but the tension in a fluid interface is a constant characteristic of the pair of fluids in contact.<sup>2</sup> Another difficulty with the viewpoint that the surface is covered with a contractile skin is that the skin does not contract when the surface decreases but rather molecules are withdrawn from the surface by the inward attractive force.

For the case illustrated, the surface tension is quantitatively equal to *W* dynes/*2l* cm, the coefficient 2 appearing because of the two faces of the film. If the barrier *l* is allowed to drop 1 cm in response to the force *W*, mechanical work equal to *W* dynes  $\times$  1 cm, i.e., *W* ergs, is performed, and *2l* cm  $\times$  1 cm,

<sup>1</sup> *Théorie mécanique de la Chaleur*, Paris (1869).

<sup>2</sup> In certain special cases, when one or both of the fluid phases are solutions, the interfacial tension may not be entirely independent of extension. Such interfaces are said to be "unsaturated" and will be referred to later. In reality, the Dupré experiment cannot be carried out so simply with pure liquids because the tension would have to be slightly greater at the top of the film than at the bottom in order to balance the weight of the film itself. Since the tension of a pure liquid is constant, a pure liquid film of appreciable size has only a temporary existence.



i.e.,  $2l$  cm<sup>2</sup> of new surface are produced by bringing molecules of the fluids from the interior of the adjacent phases into the boundary region. For each square centimeter, the mechanical work is therefore  $W/2l$  ergs, which is numerically equal to the interfacial tension expressed in dynes per centimeter. This energy remains associated with the boundary region in a potential form and becomes available for the performance of work when the boundary disappears.

Measurements of surface tension show that surface tension decreases with rising temperature, except in the case of certain metals, from which it follows<sup>3</sup> that there is an absorption of heat when the surface of a liquid is extended. Consequently, heat energy must be added to maintain constant temperature. The *total surface* (or *interfacial*) *energy*  $H_{ab}$  can be derived from the Gibbs-Helmholtz equation

$$H = F - T \left( \frac{\partial F}{\partial T} \right)_P \quad (25.1)$$

Since  $\gamma_{ab}$  is the interfacial free energy

$$H_{ab} = \gamma_{ab} - T \left( \frac{\partial \gamma_{ab}}{\partial T} \right)_P \quad (25.2)$$

where  $H_{ab}$  measures the total energy required to form 1 cm<sup>2</sup> of fresh boundary region isothermally.  $-(\partial \gamma_{ab}/\partial T)_P$  is seen to represent the surface entropy per unit area, and a study of this term yields information concerning orientation in the surface layer.<sup>4</sup>

Other useful quantities in the study of surfaces are the *free cohesive energy* ( $W_c$ ) and the *free adhesional energy* ( $W_a$ ). The free cohesive energy<sup>5</sup> is the work required to form 2 cm<sup>2</sup> of fresh interface of liquid  $b$ ; thus,

$$W_c = 2\gamma_b \quad (25.3)$$

It may be considered as the work required to pull a bar of liquid of 1 cm<sup>2</sup> cross-section asunder without change in cross section. The free adhesional energy is the work required to break a column of 1 cm<sup>2</sup> cross section consisting of two different liquids at the interface between them yielding two new interfaces. If liquid  $b$  is pulled from the liquid  $a$ , the increase in free energy is  $\gamma_a + \gamma_b$  in the ideal case in which the liquids are completely separated from each other. There is a concomitant decrease of free energy equal to  $\gamma_{ab}$ , due to the destruction of the interface  $ab$ ; thus,

$$W_a = \gamma_a + \gamma_b - \gamma_{ab}. \quad (25.4)$$

This important relation is due to Dupré.<sup>6</sup> If liquids  $a$  and  $b$  are mutually soluble to an appreciable extent, as is often the case,  $\gamma_a$  and  $\gamma_b$  must refer to saturated solutions of  $b$  in  $a$  and  $a$  in  $b$  in order that the equation may be correct.

<sup>3</sup> Thomson (Lord Kelvin), *Phil. Mag.*, 17, 61 (1859).

<sup>4</sup> Adam, *op. cit.*, p. 162.

<sup>5</sup> Harkins, *J. Am. Chem. Soc.*, 43, 55 (1921).

<sup>6</sup> Dupré, *op. cit.*, p. 369.

As it stands, Equation (25.4) expresses the free energy change when the two pure liquids are brought into contact, neglecting the energy change accompanying mutual solution.

(26) **The Determination of Surface or Interfacial Tensions:** The many methods for measuring interfacial tensions are usually classified in two groups—"static" methods which measure the tension of practically stationary surfaces which have been formed for an appreciable time, and "dynamic" methods which measure the tension of fresh surfaces which may not be old enough for adsorption to have reached equilibrium.

<i>Static Methods</i>	<i>Dynamic Methods</i>
1. Capillary Rise or Fall	1. Vibrating Drop
2. Drop Weight	2. Oscillating Jet
3. Bubble Pressure	3. Surface Ripples.
4. Adhering Ring or Plate	
5. Curvature of Free Surface	
6. Dimensions of Sessile Drop or Bubble	
7. Pendant Drop.	

Division of the methods into these two groups is, however, rather arbitrary because in some of the dynamic methods, as for example, surface ripples, there is so little renewal of the surface that the surface tension measured is the "static" tension, and measurements carried out rapidly with the ring method yield a "dynamic" tension in cases where the surface tension changes slowly with time. At present the dynamic methods do not give a quantitative measure of the time which has elapsed since the formation of the surface before the measurement is effectively taken. In the case of solutions showing pronounced adsorption, the interpretation of dynamic measurements is handicapped by the lack of information on the time factor. No attempt will be made here to describe the various methods in detail.<sup>1</sup> It should be noted that the equations usually derived for the various methods require corrections which can be calculated only approximately or determined experimentally.

The capillary rise method is at present the ultimate standard because of the high degree of approximation to which the theory has been carried and the experimental accuracy. For accurate measurements it is essential that the contact angle between glass and liquid be zero, and corrections must be applied for the curvature of the meniscus and the external reference interface.<sup>2</sup> The values of the surface tensions of water and benzene against air saturated with their vapors determined by the capillary rise method (Table IX) are used as standards in calibrating other methods. For work with small volumes the drop weight method is useful. Hauser<sup>3</sup> and others, using a high speed camera, show that the secondary small drop, formed when the long neck from which the

<sup>1</sup> For a critical and detailed discussion of the methods see especially Adam, *op. cit.*, chap. IX.

<sup>2</sup> Rayleigh, *Proc. Roy. Soc.*, A92, 184 (1915).

<sup>3</sup> *J. Phys. Chem.*, 40, 973 (1936).

TABLE IX  
 SURFACE TENSIONS OF TYPICAL MOBILE INTERFACES<sup>1</sup>

Liquid	Temperature	Surface tension, dynes/cm
<i>Pure Liquids:</i>		
Water.....	20.0°	72.80, <sup>2</sup> 72.73 <sup>3</sup>
Benzene.....	20.0	28.88
Ethanol.....	20.0	22.32
Acetone.....	20.0	23.32
Formic Acid.....	20.0	37.58
Acetic Acid.....	20.0	27.42
Propionic Acid.....	20.0	26.70
Chloroform.....	20.0	27.1
<i>Molten Metals:</i>		
Copper.....	1200°	1160
Silver.....	1100	909
Gold.....	1200	1120
Mercury.....	20	436-484
Cadmium.....	400	597-640
Lead.....	400	446
<i>Molten Glasses:</i> <sup>4</sup>		
Na <sub>2</sub> O, CaO, 6SiO <sub>2</sub> .....	1050°	474
Na <sub>2</sub> O, CaO, 5SiO <sub>2</sub> .....	1050	449
1.4 Na <sub>2</sub> O, 0.9 CaO, 0.03 BaO, 6SiO <sub>2</sub> ....	1200	312
1.4 Na <sub>2</sub> O, 0.9 CaO, 0.03 PbO, 6SiO <sub>2</sub> ....	1200	273

<sup>1</sup> Compiled from International Critical Tables I, 103, IV, 439-463, *Annual Tables of Physical Constants* (1942), No. 700.

<sup>2</sup> Harkins and Brown, *J. Am. Chem. Soc.*, **41**, 503 (1919).

<sup>3</sup> Richards and Carver, *ibid.*, **43**, 827 (1921).

<sup>4</sup> Morey, G. W., *The Properties of Glass* (New York: Reinhold Publishing Corporation, 1938).

upper part of a falling drop is drawn out breaks up, often consists of several droplets, so that it is clear why no simple drop-weight formula exists. For practical purposes the gaps in the theory have been covered by the work of Harkins and Brown,<sup>4</sup> who have empirically determined the function relating the weight of the detached drop to the interfacial tension. With these corrections the drop weight method is capable of 0.1 per cent accuracy in careful hands. The bubble pressure method is convenient and has the advantage of being independent of the contact angle. Corrections have been worked out by Schrödinger<sup>5</sup> and Sugden.<sup>6</sup> Measurements by the ring method are popular on

<sup>4</sup> *J. Am. Chem. Soc.*, **41**, 499 (1919).

<sup>5</sup> Schrödinger, *Ann. Physik*, **46**, 413 (1915).

<sup>6</sup> Sugden, *J. Chem. Soc.*, **121**, 858 (1922); **125**, 27 (1924).

account of their simplicity and convenience.<sup>7</sup> In this method a correction must be applied for the weight of liquid raised.<sup>8</sup> The downward pull on a vertical plate, without detachment, gives a very accurate measure of surface tension.<sup>9</sup> The sessile drop or bubble method is of value when changes in surface tension extending over long periods of time have to be measured,<sup>10</sup> and over a range of temperatures.<sup>11</sup>

(27) **Effect of Chemical Nature upon Interfacial Tension:** Measurements of interfacial tension have been made over a wide range of conditions of temperature and pressure and for many types of interfaces. The values fall between a small fraction of a dyne and 1,000 dynes, or more, per centimeter. The surface tensions of materials that are liquid under the ordinary conditions of temperature and pressure usually fall below 100 dynes/cm. With the exception of hydrogen peroxide, water has the highest tension of any known nonmetallic pure liquid at normal temperatures. Substances of low boiling point usually have low surface tensions; for metals, inorganic salts, and other high melting-point materials, the values are high. The presence of inert gases in contact with liquids normally does not change the surface tension more than a few per cent from that existing in presence of the vapor alone; the differences often can be ascribed to the appreciable solubility of the gas. Jaeger<sup>1</sup> has pointed out that the surface tensions of molten alkali salts (against nitrogen) reveal an approximate ionic additivity that may be expressed with few exceptions in the form of the series  $F^- > SO_4^{2-} > Cl^- > Br^- > NO_3^- > I^-$  and  $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$ . It is possible that similar series, occurring so frequently in connection with colloidal solutions containing dissolved salts and designated as "lyotropic," may be fundamentally conditioned by the same factors that determine the surface tensions of the molten salts.<sup>2</sup>

The values of interfacial tensions for liquid pairs are shown to have the same order of magnitude as for liquid||gas interfaces. The mutual solubility of the two fluids, however, cannot be disregarded so often as in the case of liquid||gas interfaces. This fact prevents a direct comparison of the interfacial tensions of one liquid with various fluid phases. Comparisons have been made, however, of the interfacial tensions of pairs of mutually saturated liquids with the tensions of the separate saturated liquids against the same vapor phase.

Antonoff's<sup>3</sup> "rule" which states that the liquid||liquid interfacial tension is equal to the difference between the surface tension of the mutually saturated

<sup>7</sup> du Noüy, *J. Gen. Physiol.*, **1**, 521 (1919); *Surface Equilibria of Colloids* (New York: Chem. Catalog Co., 1926).

<sup>8</sup> Harkins and Jordan, *J. Am. Chem. Soc.*, **52**, 1751 (1930).

<sup>9</sup> Wilhelm, *Ann. Physik*, **119**, 177 (1863); Harkins and Anderson, *J. Am. Chem. Soc.*, **59**, 2189 (1937).

<sup>10</sup> Brown, *Proc. Physical Soc.*, **48**, 312 (1936).

<sup>11</sup> Kemball, *Trans. Faraday Soc.*, **42**, 526 (1946); *Proc. Roy. Soc.*, **A187**, 53, 73 (1946); *ibid.*, **A190** (1947).

<sup>1</sup> *Z. anorg. Chem.*, **101**, 1 (1917).

<sup>2</sup> Freundlich, *Colloid and Capillary Chemistry* (1926).

<sup>3</sup> *J. chim. phys.*, **5**, 372 (1907); *Kolloid-Z.*, **59**, 7 (1932); **64**, 336 (1933).

TABLE X

RELATION OF LIQUID||LIQUID INTERFACIAL TENSIONS TO THE SURFACE TENSIONS OF THE LIQUIDS. TEST OF ANTONOFF'S RULE

	Surface tensions		Interfacial tensions	
	Oily H <sub>2</sub> O	Wet organic liquid	Observed	Calculated by Antonoff's rule
Benzene.....	62.36	28.82	35.03	33.54
Carbon disulfide.....	70.49	31.81	48.63	38.68
Methylene iodide.....	72.20	50.52	45.87	21.68
<i>n</i> -Heptyl alcohol.....	28.53	26.48	7.95	2.05
Isoamyl alcohol.....	25.92	23.56	5.00	2.36

liquids has been the subject of much controversy. Harkins and Ginsberg <sup>4</sup> (Table X) and others <sup>5</sup> have presented data which show that the rule does not hold in a number of cases.

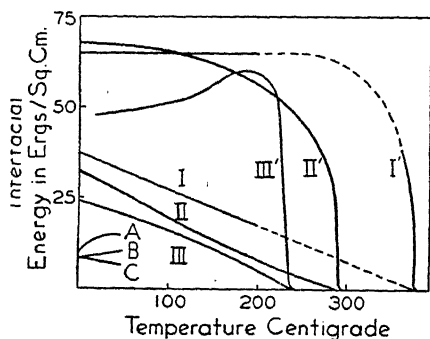


FIG. 16. Influence of Temperature upon Free (I, II, III, A, B, C) and Total (I', II', III') Interfacial Energies. Ethyl alcohol (I, I'), benzene (II, II'), and ethyl benzoate (III, III') in contact with vapor, and heptaldehyde (A), octyl alcohol (B), and heptylic acid (C) in contact with water.

(28) Effect of Temperature On Interfacial Tension: With rising temperature, the tension of a liquid ||gas interface usually decreases smoothly to zero at the critical temperature of the liquid.<sup>1</sup> Jaeger<sup>2</sup> has classified the surface tension-temperature curves into three groups (Fig. 16); the first is linear almost to the critical temperature, the second is convex, and the third is concave to the temperature axis. The curves for most pure liquids belong to the second group. The corresponding curves for the total interfacial energies, as calculated from the  $\gamma$  vs.  $T$  curves by Equation (25.2), are also of three types. In all cases, however, a smaller variation with tem-

perature makes the total interfacial energy a more suitable quantity than surface tension for comparing the surface properties of different liquids. Liquid ||liquid interfacial tensions fall to zero near a critical solution temperature; but

<sup>4</sup> Sixth Colloid Symposium (1928), p. 25.

<sup>5</sup> Miller, *J. Phys. Chem.*, 45, 1025 (1941); Carter and Jones, *Trans. Faraday Soc.*, 30, 1027 (1934); Harkins, *J. Chem. Phys.*, 9, 552 (1941).

<sup>1</sup> See Freundlich, *Colloid and Capillary Chemistry*, pp. 76-77, for some exceptions.

<sup>2</sup> *Z. anorg. Chem.*, 101, 1 (1917).

farther from the critical temperature, mutual solubility and its variation with temperature produces results that are often less regular than the temperature effect for liquid||gas interfaces. Several cases are illustrated in Fig. 16.<sup>3</sup>

(29) **Interfacial Tensions of Solutions:** The addition of a third component to one of the liquids forming a mobile interface normally changes the interfacial tension. Following Muskulus and Freundlich, one may refer to solutes which change the interfacial tension relatively slightly as "capillary-inactive." When an interfacial tension is low (not over 20 to 30 dynes/cm) most added solutes are capillary-inactive. Among the capillary-inactive solutes for the interface aqueous solution||air are numbered the following: *inorganic electrolytes*, the

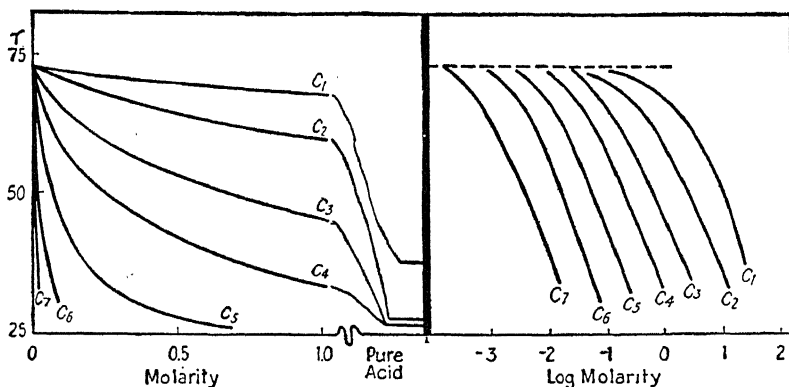


FIG. 17. Influence of Concentration upon the Surface Tensions of Aqueous Solutions of the Homologous Fatty Acids from Formic ( $C_1$ ) to Heptylic ( $C_7$ ) Inclusive.

surface tensions of which in molar solutions do not differ from that of pure water by more than a few per cent; *salts of organic acids and bases* of low molecular weight; and some *difficultly volatile nonelectrolytes* like sugar or glycerin. Solutes with high melting points often raise the surface tension, the others often lower it. Ion series (or lyotropic series) expressing the relative surface tensions of salt solutions of equal concentration resemble the series mentioned above for the molten salts themselves.<sup>1</sup>

"Capillary-active" effects usually appear as a strong depression of a relatively high interfacial tension by low concentrations of solute. The solutes which are typically capillary-active at a solution||air interface include the organic acids, alcohols, esters, ethers, amines, aldehydes, ketones, and terpenes. Figure 17, giving results obtained by Traube<sup>2</sup> and by Rehinder<sup>3</sup> for solutions of the homologous series of normal fatty acids, illustrates the capillary proper-

<sup>3</sup> From Harkins, in Alexander, *Colloid Chemistry*, Vol. I, p. 211; Harkins, Clark, and Roberts, *J. Am. Chem. Soc.*, **42**, 700 (1920).

<sup>1</sup> Freundlich, *Colloid and Capillary Chemistry*, pp. 55-60.

<sup>2</sup> *Ann.*, **265**, 27 (1891).

<sup>3</sup> *Z. physik. Chem.*, **111**, 447 (1924).

ties of solutions containing active solutes in greater detail. The surface tension-concentration curves sag strongly below the straight lines connecting the end points. Whereas the surface tension of the acid is but slightly raised by the first additions of water (i.e., capillary-inactive behavior), a very pronounced decrease accompanies the addition of small amounts of acid to water. Similar families of curves have been obtained for other homologous series of compounds. Traube found it possible to summarize the relations for many cases by means of a single rule, which can be expressed as follows:

$$\gamma_m - \gamma_s = K3^n c, \text{ as } c \rightarrow 0 \quad (29.1)$$

where  $\gamma_m - \gamma_s$  is the depression of the surface tension of the solvent  $\gamma_m$  by the concentration  $c$  of a member of a homologous series with a chain of  $n$   $\text{CH}_2$ 's, and  $K$  is a constant characteristic of the series. That is, the capillary activity,

conveniently defined as the slope of the  $\gamma$  vs.  $c$  curve at zero concentration, of such a compound is three times that of the preceding member of the series.

### (30) Variation of the Surface Tension of Solutions with Time:

The surface tension of a solution is a function of time until equilibrium is reached. At equilibrium the tendency of the kinetic agitation of the molecules in the fluid to maintain equal concentrations throughout the system is just balanced by those surface forces which tend to produce a surface composed entirely of that constituent which has the least free surface energy. The rate at which equilibrium is reached has been measured for many compounds and found to vary from a small fraction of a second to several days. The mechanism which has received the most complete treatment postulates that the time

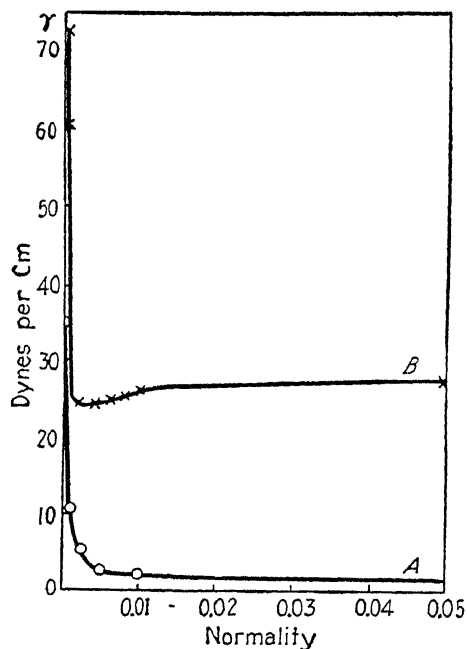


FIG. 18. A. Interfacial Tensions of Aqueous Sodium Oleate || Benzene. B. Surface Tensions of Aqueous Sodium Oleate.

effect is due to the time required for diffusion of the solute molecules to the surface.<sup>1</sup> The variation of surface tension with time has been studied

<sup>1</sup> Milner, *Phil. Mag.*, [6] 13, 96 (1907); Bond and Puls, *ibid.*, [7] 24, 864 (1937); Ross, *J. Am. Chem. Soc.*, 67, 990 (1945).

by the ring method,<sup>2</sup> the capillary rise method<sup>3</sup> and the pendant drop method.<sup>4</sup>

(31) **Capillary Behavior of the Soaps:** Exceptional capillary activity is shown by the soaps. As illustrated in Fig. 18<sup>1</sup> the surface tension drops sharply in very dilute solutions, then passes through a minimum which is followed by a region in which the surface tension increases slightly with increasing concentration. In part at least, this behavior is connected with the formation of micelles in soap solutions (p. 668) in certain concentration ranges. McBain<sup>2</sup> has pointed out that the surface tension of a dilute soap solution may be lower than the surface tension of pure oleic acid (32.5 dynes/cm) or of a water surface covered with an oleic acid monolayer (40 dynes/cm) and suggests that this is caused by the submerged double layer due to the electrolytic dissociation of the soap that is spread upon the surface. Any such double layer must lower the surface tension as illustrated by the Lippmann capillary electrometer. As the concentration of the soap is increased the dissociation of the surface molecules decreases and the surface tension increases, thus causing a minimum.

(32) **Jones-Ray Effect:** Jones and Ray<sup>1</sup> observed that in concentrations less than 0.002*N* several salts *decrease* the surface tension of water by a small amount, the maximum lowering being about 1/5000 of the tension of water. At higher concentrations the salts *raise* the surface tension almost linearly with increasing concentration, this increase being a result of the fact that there is negative adsorption and the surface layer tends to approximate pure solvent containing few of the molecules with high surface tension, i.e., those of the salt. Consequently the surface tension is raised but little above that of the solvent, even though the solute may, by itself, have a much higher surface tension than

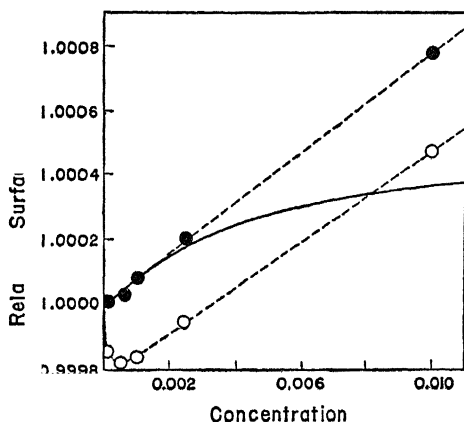


FIG. 19. Apparent and Corrected Relative Surface Tensions. Open circles are the experimental values of Jones and Ray. Solid circles are the same measurements after application of the Langmuir correction. Solid line is given by the limiting law of Onsager and Samaras. (Wood and Robinson, *loc. cit.*)

<sup>2</sup> du Noüy, *Surface Equilibria of Colloids* (New York: Chem. Catalog Co., 1926).

<sup>3</sup> Bigelow and Washburn, *J. Phys. Chem.*, **32**, 321 (1928).

<sup>4</sup> Andreas, Hauser, and Tucker, *ibid.*, **42**, 1001 (1938); Hauser, Andreas, and Tucker, *Ind. Eng. Chem.*, **31**, 32 (1939).

<sup>1</sup> Harkins, *et al.*, *J. Am. Chem. Soc.*, **39**, 541 (1917); **48**, 69 (1926).

<sup>2</sup> McBain, Ford and Wilson, *Kolloid-Z.*, **78**, 1 (1937).

<sup>1</sup> *J. Am. Chem. Soc.*, **57**, 957 (1935); **59**, 187 (1937); **63**, 288 (1941).



the solvent. Langmuir<sup>2</sup> suggested that the Jones-Ray effect was not an actual lowering of surface tension but was instrumental in origin, and advanced a quantitative theory by which the surface tension data could be corrected. He calculated that there should be a film of liquid, several hundred Å thick, on the surface of the glass capillary above the meniscus which reduces the effective radius of the capillary tube. This film would be expected to be thinner with salt solution than with pure water, so that the real radius of the tube was larger in the salt solutions than in the water, and the rise was smaller, without the tension being necessarily lower. Langmuir's interpretation has been strikingly substantiated by Wood and Robinson.<sup>3</sup> Figure 19 gives the surface tensions of dilute barium chloride solutions obtained by Jones and Ray and the tensions after the Langmuir correction. It is seen that this correction serves to eliminate the minimum from the surface tension curve and further yields surface tensions which approach infinite dilution with a slope in agreement with the limiting law of Onsager and Samaras.<sup>4</sup>

(33) **Adsorption and Gibbs's Equation:** According to thermodynamics, any process tends to occur spontaneously if it is accompanied by a decrease in free energy. If, therefore, the addition of butyric acid to water lowers the surface tension (or free surface energy) as shown in Fig. 17, it is to be expected that butyric acid will spontaneously diffuse into the interface region from the body of the liquid in order to bring about as great a reduction in free energy as possible. In analogous fashion, we should expect that water, which, added to butyric acid (Fig. 17) increases the free surface energy, will spontaneously diffuse from the interface to minimize the increase of free energy. In general, the concentration of any component in the interface region should be greater or less than in the adjacent phases according as an increase in concentration of the component decreases or increases the free interfacial energy. These two possibilities can be referred to as "positive" and "negative" adsorption.

This thermodynamic consequence was first recognized and quantitatively formulated by J. Willard Gibbs<sup>1</sup> in the differential equation

$$\partial\gamma = -\Gamma_1\partial\mu_1 - \Gamma_2\partial\mu_2 \cdots - \Gamma_n\partial\mu_n \quad (33.1)$$

where  $\gamma$  is the free interfacial energy,  $\mu_1, \mu_2, \cdots, \mu_n$  are the "chemical potentials" or partial specific free energies of the various components in the phases on both sides of the interface, and  $\Gamma_1, \Gamma_2, \cdots, \Gamma_n$  are the grams of these components that must be added to the system to maintain the corresponding chemical potentials constant when the interface is increased by 1 cm<sup>2</sup>, temperature, pressure, and any other variables being held constant, and external forces being neglected. Designating the excess (if  $\partial\gamma/\partial\mu < 0$ ) or deficiency

<sup>2</sup> *Science*, **88**, 430 (1938); *J. Chem. Phys.*, **6**, 894 (1938); *J. Am. Chem. Soc.*, **62**, 3039 (1940).

<sup>3</sup> *J. Chem. Phys.*, **14**, 258 (1946).

<sup>4</sup> *J. Chem. Phys.*, **2**, 528 (1934).

<sup>1</sup> *Trans. Connecticut Acad.*, **3** (1876); *Collected Works* (1928), Vol. I., p. 230; *J. Rice, in Commentary on the Scientific Writings of J. W. Gibbs* (New Haven: Yale University Press, 1937), Vol. I.

(if  $\partial\gamma/\partial\mu > 0$ ) of a component in the interfacial region,  $\Gamma$  therefore measures its positive or negative adsorption, as the case may be, in grams per square centimeter.

Gibbs's adsorption equation (33.1) is strikingly similar to the Gibbs-Duhem relation for the case in which the pressure is not constant

$$-\partial P + c_1\partial\mu_1 + c_2\partial\mu_2 + \cdots + c_i\partial\mu_i = 0 \quad (33.2)$$

where  $c$  is the volume concentration of each component in the bulk phase contrasted to  $\Gamma$  which is the amount of a component in a surface phase. In fact, Gibbs's analytical proof of Equation (33.1) is, *mutatis mutandis*, analogous to the analytical deduction of the Gibbs-Duhem relation. Guggenheim<sup>2</sup> has advanced new proofs for the Gibbs equation involving an easily visualized process and has introduced a concept of the surface concentration which is more easily visualized physically than that used by Gibbs. Gibbs's surface excess is a very difficult quantity to interpret physically, as it is the difference between the total amount of a component in the actual system, and that in a physically impossible system in which the two phases retain the bulk composition right up to the mathematical surface of no thickness, which can be arbitrarily placed.

The derivation<sup>3</sup> of the specific equation is simple for a binary solution in contact with an indifferent fluid. Equation (33.1) becomes

$$d\gamma = -\Gamma_1 d\mu_1 - \Gamma_2 d\mu_2 \quad (33.3)$$

If the precise position defined for the interface is fixed so that the surface excess of component one,  $\Gamma_1$ , vanishes

$$d\gamma = -\Gamma_2^{(1)} d\mu_2 \quad (33.4)$$

The activity coefficient,  $f_2$ , for component 2 is defined by the relation

$$\mu_2 = \mu_{0,2} + RT \ln f_2 N_2 \quad (33.5)$$

where  $N_2$  is its mole fraction. Substituting in Equation (33.4)

$$d\gamma = -RT\Gamma_2^{(1)} d \ln f_2 N_2 \quad (33.6)$$

or

$$\Gamma_2^{(1)} = -\frac{1}{RT} \frac{\partial\gamma}{\partial \ln f_2 N_2} \quad (33.7)$$

For dilute and ideal solutions where the concentration  $c_2$  is proportional to the mole fraction

$$\Gamma_2^{(1)} = -\frac{c_2}{RT} \frac{\partial\gamma}{\partial c_2} \quad (33.8)$$

Summarizing, when the free interfacial energy decreases with increasing activity (or concentration),  $\partial\gamma/\partial \ln f_2 N_2$  is negative, and the adsorption  $\Gamma_2$  of

<sup>2</sup> Guggenheim, *J. Chem. Phys.*, **4**, 689 (1936); *Trans. Faraday Soc.*, 397 (1940).

<sup>3</sup> The derivation given is essentially that of Adam, *The Physics and Chemistry of Surfaces* (Oxford, 1941).

solute into the interface is positive. As Fig. 17 shows,  $\partial\gamma/\partial \ln f_2N_2$  and positive adsorption may be large with capillary-active solutes. When the solute raises the free interfacial energy,  $\partial\gamma/\partial \ln f_2N_2$  is positive and small, and the adsorption is negative and small. This contrast is easy to understand. For positive adsorption the solute throughout the solution is available and may accumulate in the interface, but in negative adsorption only the relatively few molecules of the solute in the surface region are available for redistribution. For similar reasons the decidedly sagged  $\gamma$ -concentration curves are theoretically normal.

(34) **Experimental Tests of the Gibbs Equation:** Two experimental methods have been applied in the attempt to verify the Gibbs equation directly. The first, suggested by Donnan,<sup>1</sup> consists of passing bubbles of gas through a column containing a solution of a solute which is positively adsorbed. The apparatus is arranged so that the surface of the bubbles becomes fully saturated with the adsorbed substance, the bubbles are removed, and the solution obtained after their collapse analyzed. This solution has a higher concentration than the original solution, and by determining the excess concentration and estimating the total area of the bubbles, the adsorption may be compared with that calculated by the Gibbs equation. The experimental errors are naturally rather large, and although most of the results obtained for the adsorption are too high, they are in general agreement with the equation and most of the discrepancies have been explained by deficiencies of the experimental method.<sup>2</sup>

In a second experimental method introduced by McBain,<sup>3</sup> a thin layer, 0.05 to 0.1 mm thick, is rapidly cut off the surface of the solution which stands quietly in a long trough. A number of determinations carried out with this method are in agreement with the predictions of the Gibbs equation within the experimental error.

The Gibbs equation has been verified indirectly by calculating the areas per molecule of the adsorbed films on solutions. For the fatty acids,  $\partial\gamma/\partial \ln c$ , which is approximately proportional to the adsorption according to Gibbs's equation, gradually increases with concentration to constant values, which are almost uniform for the entire series of fatty acids (cf. Fig. 17). Langmuir<sup>4</sup> suggested that this theoretical maximum adsorption ( $\Gamma_{\max}$ ) represents a compact unimolecular film of oriented molecules similar to the floating, insoluble films of the higher fatty acids discussed below. The difference between  $\Gamma$  and the total surface concentration of adsorbed molecules being neglected, the average area per molecule ( $A$ ) is therefore equal to  $1/N\Gamma_{\max}$  in the saturated

<sup>1</sup> Donnan and Barker, *Proc. Roy. Soc.*, **A85**, 557 (1911).

<sup>2</sup> Lewis, *Phil. Mag.*, **15**, 499 (1908); **17**, 466 (1909); *Z. physik. Chem.*, **73**, 129 (1910); Donnan and Barker, *Proc. Roy. Soc.*, **A85**, 557 (1911); McBain and Davies, *J. Am. Chem. Soc.*, **49**, 2230 (1927); McBain and duBois, *ibid.*, **51**, 3534 (1929); Harkins and Gans, *Fifth Colloid Symposium* (1927), p. 40; *Sixth Colloid Symposium* (1928), p. 36; McBain, Wynne-Jones, and Pollard, *ibid.* (1928), p. 57; Laing, McBain, and Harrison, *ibid.* (1928), p. 63.

<sup>3</sup> McBain and Humphreys, *J. Phys. Chem.*, **36**, 300 (1932); McBain and Swain, *Proc. Roy. Soc.*, **A154**, 608 (1936).

<sup>4</sup> *J. Am. Chem. Soc.*, **39**, 1848 (1917).

film.<sup>5</sup> For acids above propionic the areas per molecule are approximately constant, averaging 30 to 32 Å<sup>2</sup>. These values are distinctly higher than the value 25.1 Å<sup>2</sup> found for films of the higher insoluble fatty acid by the film pressure method. Although some of the discrepancy may be due to the use of the approximate form of Gibbs's equation, in which concentrations replace activities, it is probable that the greater lateral cohesion in the higher fatty-acid films gives rise to a closer packing.

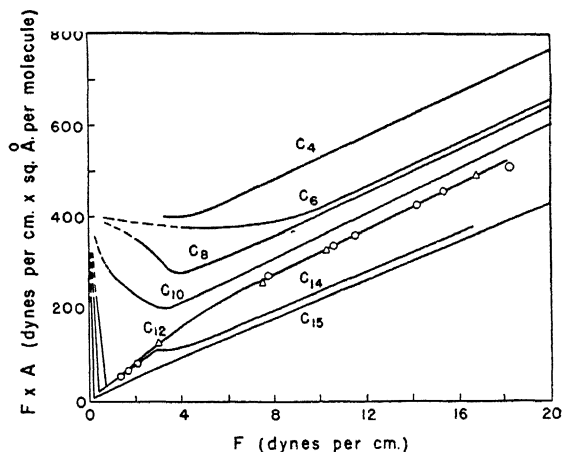


FIG. 20. Isotherms for Fatty Acid Surface Films. For the C<sub>12</sub> acid, the O points were calculated from surface tensions and the Δ points were obtained by measuring the surface pressure directly. (Adapted from Adam, *op. cit.*)

For dilute solutions of the fatty acids, the surface tension lowering  $\gamma - \gamma'$  is proportional to the concentration  $c_2$ , i.e.,

$$\gamma - \gamma' = Bc_2 \quad (34.1)$$

Differentiating and combining with the approximate form of Gibbs's equation yields

$$\Gamma_2 = \frac{Bc_2}{RT} \quad \frac{\gamma - \gamma'}{RT} \quad (34.2)$$

Since  $1/\Gamma_2$  is the surface area per mole of adsorbed solute,  $A$ , and  $\gamma - \gamma'$  is the surface pressure,  $\pi$ ,

$$\pi A = RT \quad (34.3)$$

This equation is exactly analogous to the ideal gas law  $pV = RT$ . If  $\pi$  is in dynes per cm and  $A$  in Å<sup>2</sup> per molecule,  $R$  is 400. At sufficiently low pressures this relation is followed very closely by films of the lower fatty acids as illustrated by Fig. 20. This figure gives the values calculated by Schofield and

<sup>5</sup> The adsorption is here expressed as moles per square centimeter.

Rideal<sup>6</sup> for fatty acids with chains containing 4 to 12 carbon atoms, using Frumkin's measurements of the surface tension of the solutions.<sup>7</sup> For comparison the results for the acids containing from 12 to 15 carbon atoms, determined by spreading the acid and measuring the surface pressure directly, are given. The agreement between the two methods for the C<sub>12</sub> acid is a striking experimental verification of Gibbs's equation. At higher pressures, the deviations from ideality are similar to those for ordinary gases, and the correspondingly modified equations of state may be used.

As the molecular weight of the adsorbed molecules increases, the kinetic relations gradually change from those of gases far above their critical temperatures to those of liquids and solids. At high surface pressures the two-dimensional analog of Amagat's equation for compressed gases is applicable to the adsorption region; i.e.,

$$\frac{\pi A}{kT} = \frac{B\pi}{kT} + \frac{1}{x} \quad (34.4)$$

where  $B$  represents the least area a molecule can occupy and  $1/x$  is a measure of the cohesion at a given temperature. For the normal fatty acids,  $B$  was found to be constant and equal to 24.3 Å<sup>2</sup>, in surprisingly close agreement with Adam's value of 25.1 Å<sup>2</sup> for the higher insoluble members of this series. As might be expected,  $1/x$  increases with molecular weight. A surface pressure of 1 dyne/cm on the surface of a  $N$  butyric acid solution is equivalent to a gas pressure of ca. 48 atm.<sup>8</sup>

(35) **Theory of Molecular Orientation at Interfaces:**<sup>1</sup> To explain the origin of potential differences at interfaces, Hardy<sup>2</sup> suggested that "if the stray field of a molecule be unsymmetrical, the surface layer of fluids and solids . . . must differ from the interior mass in the orientation of the axes of the fields with respect to the normal to the surface, and so form a skin on the surface of a pure substance having all the molecules oriented in the same way instead of purely in random ways. The result would be the polarization of the surface. . . ." The dependence of interfacial properties upon molecular structure and chemical constitution, from which the asymmetric fields of force presumably arises, was made evident by measurements of the adhesional energies<sup>3</sup> of various organic liquids for water. Hardy found that adhesional energies increase with the polarity of organic molecules, saturated hydrocarbons having the lowest, and alcohols, acids and esters having the highest values. No specific interpretation in terms of molecular orientation was explicitly given, however.

<sup>6</sup> *Proc. Roy. Soc.*, **A109**, 57 (1925); 110, 167 (1926).

<sup>7</sup> Frumkin, *Z. physik. Chem.*, **116**, 480 (1925).

<sup>8</sup> Schofield and Rideal, *loc. cit.*

<sup>1</sup> General references: Harkins, in Bogue, *Colloidal Behavior* (1924), Vol. I, chap. 6, and in Alexander, *Colloid Chemistry* (1926), Vol. I, chap. 8; Langmuir, *ibid.*, chap. 29, and *Colloid Symposium* (1925), p. 48; Symposium on *Physical Chemistry at Interfaces with Special Reference to Molecular Orientation*, *Trans. Faraday Soc.*, **22**, 433 (1926); Bakker, *Kapillarität und Oberflächenspannung* (Leipzig: Akademische Verlagsgesellschaft, m.b.H., 1928).

<sup>2</sup> *Proc. Roy. Soc.*, **A86**, 610 (1912); 88, 313 (1913).

<sup>3</sup> Defined on p. 570. Hardy's tables give values of  $W_a/2$ .

This step was taken by Harkins and many accurate supporting data were furnished by him and his collaborators.<sup>4</sup> A few typical examples from their results appear in Table XI and illustrate the dependence of adhesional energies upon chemical constitution. For instance, the free energy change involved in bringing 1 cm<sup>2</sup> of isopentane into contact with an equal area of water is only 37 ergs, neglecting the heats of solution. The substitution of almost any non-

TABLE XI  
ADHESIONAL AND COHESIONAL ENERGIES (IN ERGS PER CENTIMETER)  
FOR SOME ORGANIC LIQUIDS AT 20°C

	$W_a$ with water	$W_c$		$W_a$ with water	$W_c$
Isopentane.....	36.9	27.4	Methylene chloride...	71.0	53.0
Isopentene.....	53.4	34.5	Chloroform.....	67.3	54.3
Isoamyl nitrate.....	69.2	54.4	Carbon tetrachloride..	56.2	53.5
Isoamyl chloride.....	80.8	47.0	Carbon disulfide.....	55.8	64.7
Isovaleronitrile.....	84.7	52.1	.....	.....	.....
Isoamyl alcohol.....	92.5	47.6	Octyl alcohol.....	91.8	55.0
Isovaleric acid.....	94.6	50.7	Caprylic acid.....	93.7	57.6
Ethyl isovalerate.....	78.1	47.3	Ethyl pelargonate.....	77.0	56.1

hydrocarbon group for a hydrogen atom considerably increases the attraction for water, the maximum affinity in the series given appearing with the alcohol (92.5 ergs) and acid (94.6 ergs). The single oxygen atom converting isopentane into isoamyl alcohol increases the attraction for water by ca. 170 per cent. In contrast, the addition of several CH<sub>2</sub>-groups scarcely changes the adhesional energy, as is shown by the fact that the values for the three larger molecules at the end of the table are practically identical with those for the corresponding members in the isopentane series. In general, the adhesional energy for water and compounds of the type C<sub>n</sub>H<sub>2n+1</sub>X is determined primarily by the chemical nature of X.

It is commonly recognized that the hydroxyl or carboxyl group is responsible for the greater solubility in water of the alcohols or acids as compared with the corresponding hydrocarbons. With increasing length of hydrocarbon chain, the solubility falls to very low values, but the adhesional energy remains practically constant. These relations immediately become intelligible if, as Harkins<sup>5</sup> suggested, the molecules of alcohol, acid, etc., are oriented at the water boundary with the "solubilizing" group attracted by and buried in the water phase as far as the insoluble hydrocarbon chain permits. Figure 21<sup>6</sup> graphically describes the manner in which the old principle that "like dissolves like"

<sup>4</sup> Harkins, Brown, and Davies, *J. Am. Chem. Soc.*, **39**, 354 (1917); Clark and Roberts, *ibid.*, **42**, 700 (1920); Ewing, *ibid.*, 2539; Grafton, *ibid.*, 2534; Feldman, *ibid.*, **44**, 2665 (1922).

<sup>5</sup> Harkins, Brown, and Davies, *loc. cit.*

<sup>6</sup> Harkins, in Alexander, *Colloid Chemistry* (1926), Vol. I, p. 210.

may be manifested at a liquid||liquid interface containing molecules the different parts of which may be considered as having different solubilities or "affinities" for water. The order of the "affinities" of active groups for water and the corresponding orienting tendencies probably correspond to the order of the adhesional energies of a series of related compounds. For derivatives of an

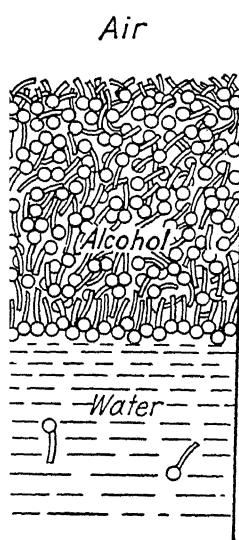


Fig. 21. Structures of the Interfaces Butyl Alcohol || Water and Butyl Alcohol || Air according to the Orientation Theory (adapted from Harkins) The circle and tail represent the OH-group and the hydrocarbon chain, respectively.

aliphatic hydrocarbon, the order is as follows: saturated paraffin < unsaturated paraffin < halides, nitrates < esters, ethers, ketones < aldehyde, amine, alcohol < acid. The groups which are responsible for the "affinity" for water are usually called "polar" groups because they confer upon the molecules containing them a characteristic permanent electric moment, which reveals itself in dielectric phenomena and in large measure probably determines the nature of intermolecular forces.<sup>7</sup> As Hardy suggested, the stray field of force surrounding such molecules has an asymmetric or at least nonspherical structure, which tends to assume special orientations in regions, such as an interface, where the external influences have a vectorial character. These conditions are not limited to liquids in contact with water, but they exist at any type of interface.

Quite similar conclusions concerning the structure of interfaces were simultaneously reached by Langmuir from a consideration of surface energies. Table XII shows that the total energy necessary to form 1 cm<sup>2</sup> of surface is practically independent of chemical composition for compounds of the type  $C_nH_{2n+1}X$  and is approximately equal to the value for hydrocarbons. But the wide variation in the adhesional energies of these compounds for water (cf. Table XI) demonstrates that the influence of the X-group upon interfacial phenomena is by no means masked by the preponderance of the hydrocarbon part of the molecule. The uniformity of the surface energies of these compounds therefore suggests, as Langmuir<sup>8</sup> pointed out, that the compositions of the surface regions are identical. This condition would exist if the X-group buried itself as far as possible in the body of the liquid, leaving the hydrocarbon chains in contact with the vapor phase (Fig. 21). In contrast with the water phase, which attracts the active groups of the organic molecule, the vapor phase is relatively nonpolar and allows the active groups to be attracted into the organic phase. The composition of the liquid||vapor boundary and its surface

<sup>7</sup> Debye, *Polar Molecules* (New York: Chem. Catalog Co., 1929); Hildebrand and Scott, *Solubility* (3d ed.; New York: Reinhold Publishing Co., 1950).

<sup>8</sup> Langmuir, *Chem. Met. Eng.*, 15, 468 (1916).

tension are therefore determined by the least active groups of the molecule. The situation is similar to that existing at the surface of a solution containing a capillary-active solute,<sup>9</sup> for in a sense the nonpolar part of the molecule in a pure liquid is a capillary-active component and is positively adsorbed in the liquid||vapor surface; the polar groups, being capillary-inactive, are negatively adsorbed. When the second phase is water, the polar groups of the organic liquid are capillary-active and are adsorbed at the interface.

TABLE XII

TOTAL SURFACE ENERGIES (IN ERGS PER CM) OF COMPOUNDS OF THE TYPE  $C_nH_{2n+1}X$ <sup>1</sup>

	Temp. range	<i>E</i> (mean)		Temp. range	<i>E</i> (mean)
<i>n</i> -Octane.....	20-40°C	51	Isoamyl alcohol.....	10-20°C	47
Diisoamyl.....	0-20	47	<i>n</i> -Octyl alcohol.....	0-20	49
<i>n</i> -Hexacontane.....	115-160	47	Myricyl alcohol.....	95-131	55
<i>n</i> -Octylene.....	2-20	52	<i>dl</i> -Methyl hexyl		
Isoamyl cyanide.....	20-60	53	carbinol.....	20-40	50
Isoamyl chloride.....	10-20	50	Ethyl ether.....	20-50	52
Isoamyl nitrite.....	14-35	45	Isoamyl ether.....	18-64	47
Isovaleraldoxime.....	20-50	55	Butyric acid.....	0-20	56
Isovaleronitrile.....	10-20	54	Isocaproic acid.....	17-46	51
Isoamyl amine.....	10-20	52	Isoamyl acetate.....	0-20	53
Diisobutyl amine.....	-70-20	48	Isobutyl isovalerate...	0-20	52
<i>n</i> -Hexyl amine.....	-18-65	47	<i>act</i> -Amyl stearate.....	30-50	52
			Tripalmitin.....	56-66	52

<sup>1</sup> Calculated from data in *International Critical Tables*.

A numerical comparison of the capillary activities of the polar and nonpolar groups of a molecule and therefore, presumably, an evaluation of the asymmetry in its field of force, may be obtained by taking the difference between the adhesional energy toward water (determined by the most polar groups) and the cohesional energy (determined, like surface tension, by the least polar groups).<sup>10</sup> Corresponding values of  $W_a$  and  $W_c$  are given together in Table XI.<sup>11</sup>

(36) **Spreading of Films:** It has already been pointed out that films form on the surface of solutions of capillary active substances. Such films may also be obtained by touching the film-forming substance to the surface or by dropping a solution of the substance in a volatile solvent on the surface. The type of film which spreads is determined by the interfacial free energy relations involved. Harkins<sup>1</sup> considers three general types of films: (1) monolayers,

<sup>9</sup> See p. 575.

<sup>10</sup> Harkins, Clark, and Roberts, *loc. cit.*

<sup>11</sup> Both Harkins and Langmuir have also discussed the more complicated orientation relations occurring in liquids such as the di-substituted benzenes, which contain several polar groups.

<sup>1</sup> The following discussion of the spreading of oil films follows Harkins, in Alexander, *Colloid Chemistry* (1944), Vol. V.



(2) films thicker than monolayers, but thinner than duplex films, and (3) duplex films, e.g., films which are sufficiently thick to give complete independence between the energy of the surface and that of the interface. If the free cohesive energy ( $W_{cb}$ ) of an oil placed on a clean water surface is greater than its free adhesive energy with water ( $W_a$ ), it will not spread. If the reverse is true, it will spread as a duplex film and the spreading coefficient is defined as

$$S_{b/a} = - \left( \frac{\partial F}{\partial \sigma} \right)_{P,T} = W_a - W_{cb} = \gamma_a - (\gamma_b + \gamma_{ab}) \quad (36.1)$$

where  $-(\partial F/\partial \sigma)_{P,T}$  is the rate of decrease of the free energy ( $F$ ) of the system with increase of area ( $\sigma$ ) of the duplex film; the final form of this equation is obtained from (25.3) and (25.4). It is necessary to distinguish between the initial spreading coefficient ( $S_{b/a}$ ), the semi-initial spreading coefficient ( $S_{b'/a}$ ) for the liquid saturated with water, and the final spreading coefficient ( $S_{b'/a'}$ ) for mutually saturated liquids. For example, in the case of benzene, the initial spreading coefficient is

$$S_{b/a} = 72.8 - (28.9 + 35.0) = 8.9 \text{ ergs/cm}^2 \quad (36.2)$$

Since there is a decrease in free energy of 8.9 ergs for each square centimeter of duplex film formed, the benzene spreads. As the thin duplex film of benzene becomes saturated with water, the spreading coefficient changes to the semi-initial coefficient, which is

$$S_{b'/a} = 72.8 - (28.8 + 35.0) = 9.0 \text{ ergs/cm}^2 \quad (36.3)$$

When the water becomes saturated with benzene, the final spreading coefficient is

$$S_{b'/a'} = 62.2 - (28.8 + 35.0) = -1.6 \text{ ergs/cm}^2 \quad (36.4)$$

The negative value indicates that benzene will not spread over the surface of water as a duplex film if the liquids are mutually saturated. However, since the surface tension has been reduced from 72.8 dynes/cm to 62.2 dynes/cm by the benzene it is covered with a non-duplex benzene film; the film pressure, given by Equation (38.1) below, is

$$\pi = \gamma_w - \gamma = 10.6 \text{ dynes/cm} \quad (36.5)$$

In the case of a paraffin oil with a molecular weight so high that it gives almost no vapor pressure at room temperature, the initial spreading coefficient has a high negative value so that no duplex film is formed, and it does not spread even as a gaseous monolayer, at least not sufficiently to give a measurable film pressure.

The free energy of a duplex film is the sum of that for the interface ( $\gamma_{ab}$ ) and for the surface of the oil ( $\gamma_b$ ). From the above discussion it is seen that if the free energy of a duplex film is greater than that of water, it will not form. If it is less than that of water, it may spread, but since the free surface energy of a monolayer (and a lens) is always less than that of the duplex film, the latter

is not stable and always transforms to a monolayer (and lens). If a duplex film cannot form, a monolayer is produced, even if the initial spreading coefficient is negative. However, such a monolayer may not give a measurable film pressure if the oil is nonpolar and does not give a measureable three-dimensional vapor pressure. Final spreading coefficients are all negative; for example, the final spreading coefficients for methylene iodide, *n*-heptyl alcohol, and benzene on water at 20°C, are -24.2, -5.9, and -1.6, respectively.

(37) **The Study of Monolayers:** The calming action of oil films on waves was known in ancient times and used in protecting ships in a rough sea. Rayleigh<sup>1</sup> was apparently the first to measure accurately the lowering of the surface tension of water covered with an oil film. He found that 0.81 mg of olive oil was required, on an area of 555 cm<sup>2</sup>, to reduce the surface tension by the amount (about 16 dynes/cm) required to stop the movements of camphor on water; the average thickness of this film was about 16 Å.<sup>2</sup> Miss Pockels<sup>2</sup> found that surface films can be handled by pushing them in front of strips or barriers extending the whole width of a trough of water, and that a water surface may be cleaned by passing barriers across it. She also observed that when the area of a film exceeded a certain critical area, the surface tension is that of clean water, and that it falls rapidly when the area is reduced below this value.<sup>3</sup> Rayleigh<sup>4</sup> suggested that at this critical area the molecules are just crowded together into a layer one molecule thick, and he estimated the diameter of a molecule of oil to be about 10 Å by this hypothesis. Similar values were obtained by Devaux<sup>5</sup> and Marcelin<sup>6</sup> with different oils by observing the areas of films on talc-covered water surfaces.

Langmuir<sup>7</sup> introduced new experimental methods of great importance to the study of films. He measured the outward surface pressure of the film directly with a balance to be described in the next section. Pure substances of known constitution were used in place of "oils," and both the thickness of the film and the average area occupied by one oil molecule were calculated in accordance with Rayleigh's assumptions of the unimolecular nature and the normal density of the film. The results of these calculations are given in Table XIII. Langmuir found that the area per molecule is approximately constant for the saturated acids and alcohols over a considerable range in length of the hydrocarbon chains. It is evident that the film thickness increases with increase in molecular weight or number of carbon atoms for the same type of compounds. According to the last column of the table, the increment in film thickness for each additional C in the length of the molecule is of the same order

<sup>1</sup> Rayleigh, *Proc. Roy. Soc.*, **A47**, 364 (1890).

<sup>2</sup> *Nature*, **43**, 437 (1891).

<sup>3</sup> The oils used in the earlier researches formed coherent films. In the case of gaseous films, in which the molecules move independently, the surface tension decreases gradually from the largest areas.

<sup>4</sup> *Phil. Mag.*, **48**, 337 (1899).

<sup>5</sup> *J. phys. rad.*, **3**, 450 (1904); **2**, 699, 891 (1912).

<sup>6</sup> *Ann. phys.*, **1**, 19 (1914).

<sup>7</sup> *J. Am. Chem. Soc.*, **39**, 1848 (1917).

of magnitude but distinctly less than the minimum distance between C-atoms in diamond, i.e., 1.54 Å. Langmuir therefore concluded that these molecules are actually the much elongated structures pictured by the organic chemists' structural formulas, and further, that they spread on a water surface to form an oriented, unimolecular film in which the long axis of the molecule is approximately perpendicular to the plane of the film. The "area per molecule" and the "film thickness" accordingly measure the cross-section and the length of the molecules. These results provided the first direct evidence demonstrating that organic molecules actually possess the shape and proportions indicated by their structural formulas.

TABLE XIII  
CROSS-SECTIONS AND LENGTHS OF MOLECULES AS ESTIMATED BY LANGMUIR

	C-atoms per molecule	Film thickness	Area per molecule	Molecular length per C-atom
Palmitic acid.....	16	24.0 Å	21 Å <sup>2</sup>	1.50 Å
Stearic acid.....	18	25.0	22	1.39
Cerotic acid.....	26	31.0	25	1.20
Tristearin.....	57	25.0	66	1.32
Oleic acid.....	18	11.2	46	0.62
Triolein.....	57	13.0	126	0.69
Trielaidin.....	57	13.6	120	0.72
Cetyl palmitate.....	32	41.0	23	2.56
Myricyl alcohol.....	31	41.0	27	1.37

To explain the occurrence of orientation in such films, Langmuir independently introduced the idea used by Harkins in interpreting interfacial tension: namely, the active or polar group of the molecule, e.g., the  $-\text{COOH}$  of an acid or the  $-\text{OH}$  of an alcohol, is attracted by the water substratum and dissolves therein as far as the insolubility of the attached hydrocarbon chain or chains permit. When the insoluble molecules of the film are closely packed together, they stand upright so that the maximum number of active groups can bury themselves in the water phase. If the hydrocarbon chains are long, the lateral cohesion between them prevents their separation. This theory offers a simple interpretation of the relations implied in Table XIII: the approximate constancy in the average area occupied by long, normal hydrocarbon chains terminated by an active group, regardless of the active group or the length of the chain; the regular increase in film thickness with increasing length of the hydrocarbon chain; the simple multiple relation between the areas occupied by stearic acid and tristearin molecules or between the areas of oleic acid and triolein or trielaidin; and the increase in the area per molecule due to a second active group, as the double bond in oleic acid and its derivatives.<sup>8</sup>

<sup>8</sup> Adam (*op. cit.*) claims that the larger area is due to the "expanded" condition of the oleic acid film at the temperature of experimentation.

(38) **Measurement of Film Pressure:** Surface films resist compression because of the repulsion between the film molecules. This repulsion between the film molecules diminishes the surface tension of the water surface covered by film. Thus surface films may be studied by measuring the pressure which they exert on the barrier of a film-pressure balance or by measuring the surface tension of the film-covered surface. The relationship between the surface pressure of the film and the surface tension of the film-covered surface is derived in the following simple way by Adam.<sup>1</sup> If the floating barrier of a film-pressure balance is displaced a small distance  $dx$  away from the film-covered surface and toward the clean water surface, then the work done on it by the surface pressure  $\pi$  is  $\pi l dx$ , where  $l$  is the length of the float. But if  $\gamma$  is the surface tension of the clean water surface and  $\gamma'$  that of the film-covered surface, an area  $l dx$  of free energy  $\gamma$  has been replaced by one of free energy  $\gamma'$ , and the work done must be  $(\gamma - \gamma') l dx$ . These two expressions for the work must be equal; hence

$$\pi = \gamma - \gamma' \quad (38.1)$$

Thus the film pressure is equal to the diminution of the surface tension of water by the film. Harkins and Anderson<sup>2</sup> have pointed out that the film pressure does not act in a horizontal plane against the edge of the floating barrier but at an angle. However, by a mathematical analysis they were able to show that the method gives a correct value of  $\gamma - \gamma'$ .

**Surface Balance Method:**<sup>3</sup> The lateral pressure of a surface film may be measured with an apparatus originally introduced by Langmuir.<sup>4</sup> In this apparatus, which is illustrated in Fig. 22, the horizontal tray is covered with a surface which is not wet by water, and it is filled with clean water to a level somewhat higher than the edges. The moveable barriers  $A$  are used to "sweep" impurities off the water surface and to confine the film floating between  $A$  and  $B$ . The latter is a light floating barrier attached to a torsion balance which is used to measure the pressure. An improvement introduced by Adam and Jessop<sup>5</sup> was to connect the ends of the barrier to the sides of the tray with thin

<sup>1</sup> Adam, *op. cit.*

<sup>2</sup> *J. Am. Chem. Soc.*, 59, 2189 (1937).

<sup>3</sup> Adam, *Proc. Roy. Soc.*, A99, 336 (1921); 101, 452, 516 (1922); 103, 676, 687 (1923); 119, 628 (1928); Adam and Dyer, *ibid.*, 106, 694 (1924); Adam and Jessop, *ibid.*, 110, 423, 441; 112, 362, 376 (1926); 120, 473 (1928); *Trans. Faraday Soc.*, 22, 472, 494, 497 (1926); Adam, Berry, and Turner, *Proc. Roy. Soc.*, A117, 532 (1928). Summaries: Adam, *J. Phys. Chem.*, 29, 87 (1925); *Chem. Rev.*, 3, 163 (1926); *Trans. Faraday Soc.*, 24, 149 (1928). Surface-pressure balances have also been used by Marcelin, *Compt. rend.*, 173, 38 (1921); 175, 346 (1922); 176, 502; 177, 41 (1923); 178, 1079 (1924); *Ann. phys.*, 4, 459 (1925); Harkins and Morgan, *Proc. Nat. Acad. Sci.*, 11, 637 (1925) (polymolecular films); Delaplace, *J. phys. rad.*, 9, 111 (1928); Katz and Samwel, *Ann.*, 472, 241 (1929) (cellulose derivatives); Gorter and Grendel, *Proc. Acad. Sci. Amsterdam*, 29, 1262 (1926); *Trans. Faraday Soc.*, 22, 477 (1926); *Biochem. Z.*, 192, 431; 201, 391 (1928) (proteins and fats); Lyons and Rideal, *Proc. Roy. Soc.*, A124, 322, 333, 344 (1929).

<sup>4</sup> *Loc. cit.*

<sup>5</sup> *Loc. cit.*

gold or platinum strips so as to prevent leakage of the compressed film. The spreading tendency of the film is compensated by a force on the barrier so that the moveable barrier is maintained at its zero point.

*Surface Tension Method:* In this method the surface tension of the film-covered surface is determined by measuring the vertical downward pull upon a thin sheet of solid material, such as glass, quartz or metal, which is partially immersed in the liquid. This type of apparatus was introduced by Wilhelmy <sup>6</sup>

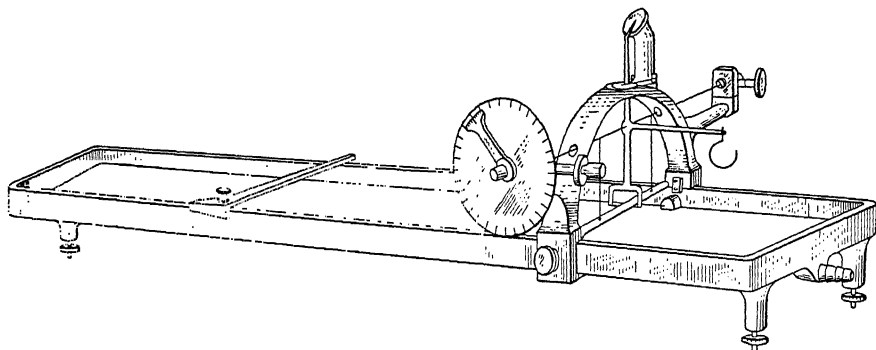


FIG. 22. Film Balance. (From Daniels, Mathews, and Williams, *Experimental Physical Chemistry*.)

to measure the surface tension of liquids, and as a differential method it is extremely sensitive, making it possible to measure film pressures of 0.001 dyne/cm or less. This method is more convenient than the film-balance method for measuring the film pressure of a soluble film, and it is especially useful in investigations in which ions of the metals have a deleterious effect because both the tray and slide may be made of quartz. If  $G$  is the "apparent" weight in grams of a slide partly immersed in water and  $w$  is the width of the slide and  $t$  its thickness, the vertical pull of the surface tension on the slide is  $2(t + w)$  if the contact angle is zero. The buoyant force on the slide, equal to the weight of the water displaced, is  $-gdltw$ , where  $g$  is the acceleration of gravity,  $d$  is the density of the liquid, and  $l$  is the depth of immersion of the slide. If  $W$  is the mass of the free dry slide and  $G$  is the "apparent" mass of the partially immersed slide,

$$gG = gW + 2\gamma(t + w) - gdltw \quad (38.2)$$

If the weight  $G$  is held constant while the surface tension is reduced  $\Delta\gamma = \pi$  by the spreading of the film, the slide rises  $\Delta l$  cm and a measurement of this quantity makes it possible to measure the film pressure,  $\pi$ ; thus,

$$\pi = \frac{gdwt}{2(t + w)} \Delta l \quad (38.3)$$

<sup>6</sup> *Ann. Physik.*, 119, 177 (1863).

The force which is exerted on the movable barrier of the film balance has been interpreted in two different ways. Both of these viewpoints have been useful in the development of surface chemistry and each has been upheld by various investigators.<sup>7</sup> According to the kinetic viewpoint, the pressure exerted by the film is exactly analogous, in the two dimensions of the surface, to osmotic pressure in three dimensions. The float is here the "semipermeable membrane" which renders the "osmotic pressure" exerted by the molecules of the film measurable. According to the surface tension viewpoint, the barrier is pulled toward the clean water surface by the surface tension of the water which tends to reduce its surface area, and it is being pulled toward the film-covered surface in the opposite direction, but not as strongly because the film lowers the surface tension of water.

*Surface Potentials:* The potential difference between a small metal plate held above the water surface in a spreading trough and a reversible electrode located in the water may be measured with a potentiometer or electrometer if the air under the electrode is made into an electrically conducting medium by a trace of radioactive material on the electrode.<sup>8</sup> This potential is altered if a film is formed on the clean water surface, and this change in potential, which may be as large as 0.9 volt, is called the "surface potential" of the film. In another method<sup>9</sup> for measuring surface potentials a horizontal metal plate above the surface is made to vibrate 250 to 500 times per second and the resulting current flow used to locate equipotentials. In the case of heterogeneous films, as myristic acid monolayers at areas greater than 52 Å<sup>2</sup> per molecule,<sup>10</sup> the surface potential varies from point to point over the film which consists of islands of liquid-expanded film in a sea of gaseous film. Surface potential measurements are therefore useful in studying the homogeneity of a film. The surface potential is more difficult to interpret in terms of molecules. It is customary to draw the analogy between the electrical double layer at the surface and a plane parallel condenser. In terms of Helmholtz's equation,<sup>11</sup> the surface potential,  $\Delta V$  is

$$\Delta V = 4\pi n\mu, \quad (38.4)$$

where  $n$  is the number of molecules per square centimeter of the film, and  $\mu$  is their vertical dipole moment assuming the dielectric constant is unity. Dipole moments calculated from surface potentials are considerably smaller than those found by ordinary methods which probably indicates that the structure of the electrical double layer is complicated, e.g., by the interaction between the polar groups in the film and the water molecules,<sup>12</sup> so that this simple theory cannot be applied directly.

<sup>7</sup> For example, see Adam, *The Physics and Chemistry of Surfaces* (1930), footnote 1, p. 30; and Harkins, in Alexander, *Colloid Chemistry* (1944), Vol. V, p. 38.

<sup>8</sup> Guyot, *Ann. phys.*, (10), 2, 506 (1924); Frumkin, *Z. physik. Chem.*, 116, 485 (1925).

<sup>9</sup> Zisman, *Rev. Sci. Inst.*, 3, 7 (1932); Zisman and Yamins, *Physics*, 4, 7 (1933); Yamins and Zisman, *J. Chem. Phys.*, 1, 656 (1933).

<sup>10</sup> Harkins and Fischer, *J. Chem. Phys.*, 1, 852 (1933).

<sup>11</sup> Schulman and Rideal, *Proc. Roy. Soc. A130*, 259, 270, 284 (1930).

<sup>12</sup> Harkins and Fischer, *loc. cit.*

(39) **Phase Relations of Monolayers:** The various monolayers studied may be divided into six classes as shown in Table XIV. Phases I, IV, and VI are in many respects analogous to three-dimensional gases, liquids, and solids,

TABLE XIV<sup>1</sup>  
CLASSES OF MONOLAYERS

Class	Compressibility $k = -\frac{1}{\sigma} \frac{\partial \sigma}{\partial \pi}$
I. Gas.....	ca. 0.04
II. Expanded liquid (liquid of high compressibility).....	0.02–0.07
III. Intermediate or transition phase (liquid of extremely high compressibility).....	0.2–0.5
IV. Condensed liquid (liquid of low compressibility).....	0.005–0.010
V. Superliquid phase (extremely low compressibility).....	0.0005–0.0017
VI. Solid phase.....	0.0005–0.001

<sup>1</sup> For a more complete description of these phases see Harkins, in Alexander, *Colloid Chemistry* (New York: Reinhold Publishing Co., 1944), Vol. V.

respectively, while the three other phases show no direct analogy to three-dimensional systems. The vaporization of the solid, condensed liquid, or expanded films is a transformation of the first order since there is a discontinuity in the area of the film with respect to pressure and a latent heat of vaporization. The other transformations are second order since there are discontinuities only in the heat capacity and the compressibility.

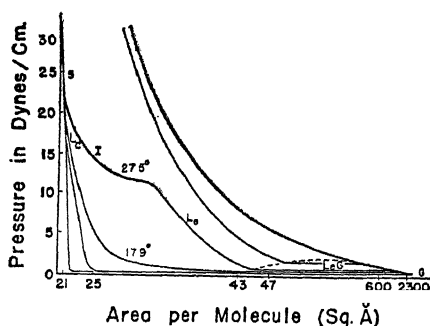


FIG. 23. Pressure-Area Isotherms. General phase diagram of a monolayer at a temperature below the critical temperature for the formation of the liquid expanded film ( $L_e$ ).  $S$  = Solid;  $L_c$  = liquid condensed;  $I$  = intermediate;  $L_cG$ , gaseous film and  $L_e$  film in equilibrium;  $G$  = gaseous film. No distinction is made here between the solid and superliquid phases. (Adapted from Harkins.)

of oleic acid, when dipped into water covered with such a layer. The monolayer, which is deposited when the plate is removed from the solution increases the contact angle of a drop of water placed on the slide. Blodgett<sup>2</sup> found that in the case of stearic acid spread on solutions containing

Figure 23 is a general phase diagram illustrating these phases. The temperatures given are correct for pentadecylic acid, but are lower for acids with a lower, and higher for acids of a higher chain length.

(40) **Built-up Films:** In studies on purification of minerals by flotation processes, Langmuir<sup>1</sup> observed that a clean glass slide becomes covered with a monomolecular layer

<sup>1</sup> *Trans. Faraday Soc.*, 15, 62 (1920).

<sup>2</sup> *J. Am. Chem. Soc.*, 56, 495 (1934); *ibid.*, 57, 1007 (1935).

calcium ions, the glass slide became covered with a double layer, one molecular layer being contributed during the down-trip and one during the up-trip. The application of these built-up films is greatly facilitated by the use of a so-called "piston oil" which applies a constant pressure to the film as it is transferred to the solid surface. Convenient "piston oils" are prepared by diluting partially oxidized lubricating oil with petrolatum,<sup>3</sup> and such oils have the property that the molecules of the oil spread on water until they have covered all the available area with a monomolecular layer, crowding together in this layer until they have established an equilibrium surface pressure. Further development of the method has made it possible to deposit more than 200 layers on glass and on various metals. Several types of built-up films may be distinguished. The monolayer, floating on the hydrous substratum is referred to as the H-layer. A layer deposited on a solid by a down-trip through an H-layer will be oriented so that the hydrophobic tails are directed inward toward the solid and such a layer is designated as an A-layer. The latter, however, are difficult to obtain as they tend to escape when the plate is withdrawn if the water surface is cleaned before the up-trip. If the plate covered with an A-layer is withdrawn through a film-covered surface, a second monolayer is deposited, this time with the hydrophobic tails directed outward. This layer, which is referred to as a B-layer, is not wet by water so that the slide emerges dry. After this process has been repeated several times, the film may be symbolized by PRABAB . . . where P stands for the plate and R the rubbed-down ferric stearate layer on the plate. With proteins PRAAA and PRBBB layers may also be prepared.<sup>4</sup> A monolayer may also be deposited by lowering the plate face downward upon the top surface of the protein monolayer. A film so deposited has been termed a lifted film, symbolized by A<sub>L</sub>.

*Measurement of Film Thickness:* Blodgett and Langmuir<sup>5</sup> and Rothen<sup>6</sup> have developed optical methods for determining the thickness of transferred films. In the first method some fifty odd layers of barium stearate are deposited on a polished metal slide in a stepwise fashion with two or four layers per step. When such a plate is observed by reflected linearly polarized monochromatic light, interference between light reflected from the air-film interface and the film-metal interface is obtained where the added thickness is of the order of a quarter of the wavelength of the light. The measurement depends on the determination of the angle of incidence at which two adjacent fields appear equally dark. When a film of unknown thickness is then deposited on the plate covered with the optical gauge the angle of incidence must be shifted to re-establish equal illumination of two adjacent steps. This shift in the angle of incidence is a measure of the thickness of the film and the optical thickness may be determined with an accuracy of about 10 Å. The method developed by Rothen is based on the observation by Drude<sup>7</sup> that the thickness of films, a few

<sup>3</sup> Blodgett, *J. Opt. Soc. Am.*, **24**, 313 (1934).

<sup>4</sup> Langmuir and Schaefer, *Chem. Rev.*, **24**, 181 (1939).

<sup>5</sup> Blodgett and Langmuir, *Phys. Rev.*, **51**, 964 (1937).

<sup>6</sup> *Rev. Sci. Instr.*, **16**, 26 (1945).

<sup>7</sup> *Ann. Physik.*, **39**, 481 (1890).



Å thick, covering a polished metallic surface could be determined by measuring the ellipticity of the light after reflection from the surface. Linearly polarized light vibrating at 45° to the plane of incidence is reflected from a polished metal plate covered with film, and the elliptically polarized light which is reflected passes through a  $\lambda/4$  plate and an analyzing Nicol prism. The difference in the position of the analyzer before and after deposition of the film is a measure of its thickness which can thus be determined within  $\pm 0.3$  Å.

*Protein Films:* <sup>8</sup> Properly spread protein films have the properties of gaseous films at pressures below 1 dyne/cm, and Guastalla <sup>9</sup> was the first to calculate the molecular weight of the protein molecules in such spread films. If the area  $A$  of the film is given in square meters per milligram of protein, the molecular weight is

$$M = \frac{24.6 \times 10^2}{\pi A} \quad (40.1)$$

Although egg albumin has the same molecular weight on the surface as in solution, hemoglobin and  $\beta$ -lactoglobulin appear to dissociate on the surface. Other evidence also indicates that the steric architecture of the protein molecule is lost in spreading.

Schaefer <sup>10</sup> has described a very simple method which serves to classify a protein monolayer into three general classes. It involves the formation of the protein monolayer, followed by the expansion of its central region with a spreading oil which reveals the degree of cohesion by which the units in the monolayer are joined to each other. The expansion patterns are star-like (egg albumin), rough circular (papain), or smooth circular (insulin) in order of decreasing viscosity.

#### IMMOBILE INTERFACES <sup>1</sup>

(41) **Adsorption:** As early as 1777, Scheele and Fontana independently observed that charcoal combines with gases and vapors with a reduction in total volume, and Lowitz in 1791 removed colored materials from solution with the same solid. Although similar qualitative observations were recorded from time to time, very little accurate information concerning the nature of the process, called "adsorption" by du Bois-Reymond, was obtained until over a

<sup>8</sup> For reviews on this subject see Bull, in *Advances in Protein Chemistry* (New York: Academic Press, 1947), p. 95; Rothen, *ibid.*, p. 123; Neurath and Bull, *Chem. Rev.*, **23**, 391 (1938); Langmuir and Schaefer, *ibid.*, **24**, 181 (1939).

<sup>9</sup> *Compt. rend.*, **208**, 1078 (1939).

<sup>10</sup> *J. Phys. Chem.*, **42**, 1089 (1938).

<sup>1</sup> McBain, *The Sorption of Gases and Vapors by Solids* (London: Routledge, 1932); Langmuir, *Chem. Rev.*, **13**, 147 (1933); Emmett, in Kraemer, *Advances in Colloid Science* (New York: Interscience Publishers, 1942), Vol. I; Brunauer, *The Adsorption of Gases and Vapors* (Princeton: Princeton University Press, 1943), Vol. 1; Deitz, *Bibliography of Solid Adsorbents* (Washington, D. C.: 1944), gives an annotated bibliography of 6002 references covering 1900 to 1942; Harkins and Jura, in Alexander, *Colloid Chemistry* (1946), Vol. VI, p. 1. An excellent review of the field as it stood at the end of 1948 is to be found in an article by Taylor, *Frontiers in Chemistry* (New York: Interscience Publishers), Vol. VIII, p. 1.

half century later. This early work has been reviewed by Freundlich<sup>1</sup> who himself contributed much to the field.

The molecules that disappear from the fluid phase either enter the inside of the solid, or remain on the outside, attached to its surface. The former phenomenon is called absorption, the latter adsorption. If the two occur simultaneously, the process is called "sorption."<sup>2</sup> Adsorption is the phenomenon in which we are interested here, and the gas (or solute from a solution) which is attached to the surface of a solid is designated the adsorbate. The adsorbate molecules may be held on the surface of the solid by a variety of different forces: electrostatic or Coulomb forces, exchange or homopolar valence forces, van der Waals forces, etc. These are the same forces which are effective in holding together the solid, and as in the case of liquids (p. 568) an atom in the plane of the surface is subjected to unbalanced forces, the inward pull being greater than the outward forces. This results in a tendency to decrease the surface, and any process that tends to decrease the surface free energy occurs spontaneously. An atom or a molecule of the gas adsorbed by the surface saturates some of the unbalanced forces of the surface, thereby decreasing the surface tension.<sup>3</sup> Thus adsorption is spontaneous and results in a decrease in the free energy of the system. Prior to adsorption the gas molecules moved freely in three dimensions, but on the surface they are restricted to two dimensions, at most, so that the adsorption process is accompanied by a decrease in entropy. According to the thermodynamic relationship

$$\Delta H = \Delta F + T\Delta S \quad (41.1)$$

$\Delta H$ , in this case called the "heat of adsorption," must also be negative. Hence all adsorption processes are exothermic, and the magnitude of the heat of adsorption yields information as to the type of forces involved. If the attractive forces are weak and of the same order of magnitude as those active in condensation, the term "physical adsorption" or "van der Waals adsorption" is applied. For example, the heat of adsorption of nitrogen on an iron catalyst is about 2 to 3 kcal per mole at  $-195^{\circ}\text{C}$ , compared to 1.36 kcal per mole which is the heat of liquefaction of nitrogen gas. If the attractive forces are strong, comparable to those involved in chemical reaction, the term "chemisorption" or "activated adsorption"<sup>4</sup> is applied. For example, the heat of chemisorption of nitrogen on iron is about 35 kcal per mole. In this case the nitrogen molecules are dissociated into atoms and only one chemisorbed layer can form on the surface, while in van der Waals adsorption nitrogen molecules are adsorbed

<sup>1</sup> Freundlich, *Colloid and Capillary Chemistry* (1926).

<sup>2</sup> McBain, *Phil. Mag.*, (6), 18, 916 (1909).

<sup>3</sup> Although no experimental procedure has been devised for the determination of the free surface energy of a clean solid surface, the Gibbs equation can be used to calculate the decrease of the free surface energy caused by the adsorption of a gas or vapor; see, Harkins and Jura, *J. Am. Chem. Soc.*, 66, 919 (1944).

<sup>4</sup> The term activated adsorption which was introduced by H. S. Taylor, *J. Am. Chem. Soc.*, 53, 578 (1931), implies that this type of adsorption requires an appreciable activation energy, just as chemical reactions do.

TABLE XV  
DESORPTION OF OXYGEN FROM CARBÓN

Temperature	Product on desorption	$\Delta H$
-150°C	O <sub>2</sub> on evacuation	3.7 kcal/mole
25°C	Only partially desorbed on evacuation	70
400°C	CO <sub>2</sub> + CO	200
600°C	CO	—

and several layers may be built up on the surface (multilayer adsorption). As in setting the limits of the colloidal size range, any sharp demarcation between van der Waals adsorption and chemisorption must be arbitrary because the differences are differences in degree and not in kind. However, some adsorption may be definitely placed in one class or the other. Under conditions in

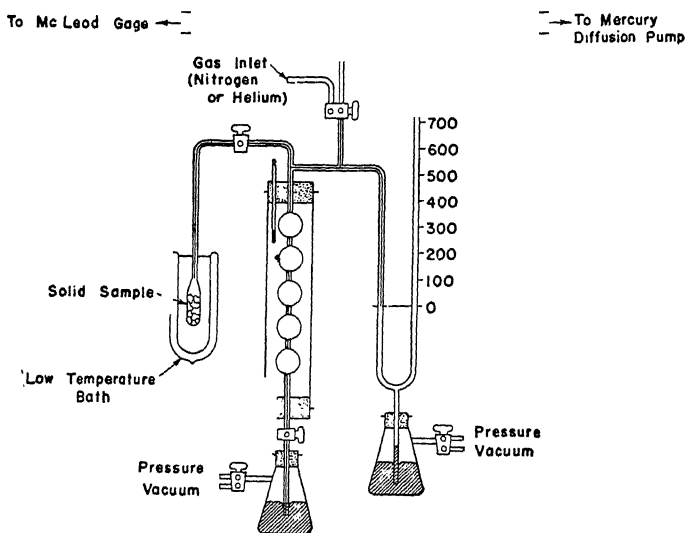


FIG. 24. Gaseous Adsorption Apparatus. (Emmett, in *Advances in Colloid Science*.)

which the two adsorptions occur simultaneously, they are usually separated on the basis of the difference in their reversibility with respect to temperature and pressure. The removal of chemisorbed gas from the surface is usually difficult, while physical adsorption is readily reversible. Table XV illustrates the transition from one type to the other for the adsorption of oxygen on carbon.<sup>5</sup>

<sup>5</sup> Langmuir, *J. Am. Chem. Soc.*, **38**, 2221 (1916); Keyes and Marshall, *ibid.*, **49**, 156 (1927); Shak, *J. Chem. Soc.*, 2661 (1922).

Chemisorption in the presence of van der Waals adsorption may also be detected by studies of isotope exchange reactions<sup>6</sup> or by the measurement of magnetic susceptibility.<sup>7</sup> The detection of hydrogen isotope exchange ( $\text{H}_2 + \text{D}_2 = 2\text{HD}$ ) at temperatures as low as  $-190^\circ\text{C}$  on surfaces such as nickel and chromium oxide gel constitutes an extremely delicate test of chemical interaction between surfaces and reacting molecules. This reaction is not ascribable to van der Waals forces, since these forces do not affect such reactions in compressed gaseous or liquid hydrogen systems. The reaction constitutes a test for chemisorption occurring in a temperature range where adsorption measurements alone fail, owing to the extensive van der Waals adsorption simultaneously occurring. At  $-190^\circ\text{C}$  the activation energy is apparently smaller than that effective at higher temperatures. Either areas of the surface where low energies of desorption obtain are involved, or some other mechanism, e.g., collision of impinging molecules with adsorbed hydrogen, is responsible for such low-temperature conversion.

By measurements of the magnetic susceptibility of charcoal on which oxygen was adsorbed Juza and Langheim<sup>8</sup> concluded that the oxygen was being chemisorbed slowly at room temperature. The strong paramagnetism of molecular oxygen slowly diminishes owing, presumably, to chemical combination between the oxygen and the charcoal. It is possible to obtain the temperature coefficient of this reaction, and the calculated activation energy of surface oxide formation is about 5 kcal/mole.

(42) **Methods of Measurement:** The amount of gas adsorbed may be determined by measuring the volume of gas taken up or by weighing the adsorbent plus adsorbed gas at equilibrium. A typical adsorption apparatus for making measurements by the first method is illustrated in Fig. 24, and the sorption balance used in the second method is illustrated in Fig. 25. The volumetric apparatus includes an adsorption bulb, a calibrated gas buret, a manometer, a high vacuum oil pump and Langmuir diffusion pump and a McLeod gauge. Before the experiment the sample of adsorbent is evacuated at a temperature sufficient to remove water vapor and physically adsorbed gases, and the "dead space" in the adsorption bulb up to the stop-cock is then determined with pure helium for which the adsorption is negligible at temperatures of  $77^\circ\text{K}$  or higher. The adsorbate is then introduced, and at

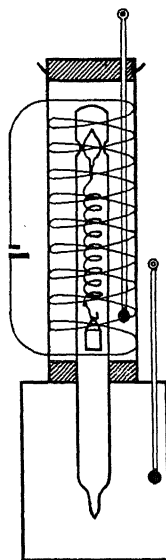


FIG. 25. Sorption Balance for Studying Gaseous Adsorption. (McBain and Bakr.)

<sup>6</sup> Taylor, in *Frontiers in Chemistry*, ed. by Burk and Grummitt, Interscience Publishers, New York, Vol. III, 1945.

<sup>7</sup> Selwood, *Chem. Rev.*, **38**, 41 (1946).

<sup>8</sup> *Naturwissenschaften*, **25**, 522 (1937); *Z. Elektrochem.*, **45**, 689 (1939).

equilibrium the volume  $V_a$  of gas adsorbed is calculated by the equation

$$V_a = V_t - V_h(1 + \alpha) - V_b \quad (42.1)$$

where  $V_t$  is the total volume of adsorbate which has been introduced into the system,  $V_h$  is the volume of adsorbate required to fill the dead space to the pressure of the experiment,  $\alpha$  is the correction factor which takes into account the gas imperfection of the adsorbate at the low temperature being used, and  $V_b$  is the volume of adsorbate remaining in the buret at the time of measurement. By adding successive amounts of adsorbate through the buret system, the adsorption at a series of pressures at the same temperature may be measured.

In the sorption balance method developed by McBain and Bakr<sup>1</sup> the adsorbent is placed in a bucket suspended on a helical spring made of fused silica which has been calibrated so that the weight may be determined accurately by its extension. During the experiment the pressure is varied by placing the lower part in a thermostat and varying its temperature. The temperature of the adsorption is fixed by thermostating the upper part of the tube. The main source of error in this method is the buoyancy correction which may be rather large at high pressures.

For a given gas and unit weight of a given adsorbent the amount  $a$  of gas adsorbed at equilibrium, in the absence of hysteresis effects (page 607), is a function of the final pressure and temperature, i.e.,  $a = f(p, T)$ . When the pressure of the gas is varied, and the temperature is kept constant, the plot of the amount adsorbed against the pressure is called the adsorption *isotherm*, and the isotherm equation is  $a = f(p)$ . When the temperature is varied and the pressure is kept constant, the adsorption *isobar* is  $a = f(T)$ . When the temperature is varied, and the amount of gas adsorbed is kept constant, the adsorption *isostere* is  $p = f(T)$ . The adsorption isotherms, isobars, and isosteres for ammonia on charcoal from  $T = 250^\circ$  to  $424^\circ\text{K}$  and  $p = 0$  to 760 mm are given in Fig. 26.<sup>2</sup>

As the isotherms show, the adsorption increases with pressure except that at high pressures the adsorbent may become saturated. At small adsorptions the volume adsorbed, measured at S.T.P., increases linearly with pressure, obeying Henry's law

$$v = kp \quad (42.2)$$

At higher adsorptions, the volume becomes proportional to a power of the gas pressure smaller than unity

$$v = k'p^m \quad (42.3)$$

where  $m$  may have values from unity, corresponding to Henry's law, to small fractions. This equation is generally referred to as the Freundlich isotherm equation, although Freundlich was not its originator. The criterion for applicability of this equation is the linearity of the relation between  $\log v$  and  $\log p$ . Although this equation is useful as an interpolation formula within a limited

<sup>1</sup> *J. Am. Chem. Soc.*, **48**, 690 (1926).

<sup>2</sup> Data of Titoff, *Z. physik. Chem.*, **74**, 641 (1910).

concentration range, it does not reproduce the phenomena observed at higher pressures. The modern isothermal relationships are discussed on p. 602.

As illustrated by the isobar in Fig. 26, the amount adsorbed at equilibrium must always decrease with increasing temperature, according to the principle

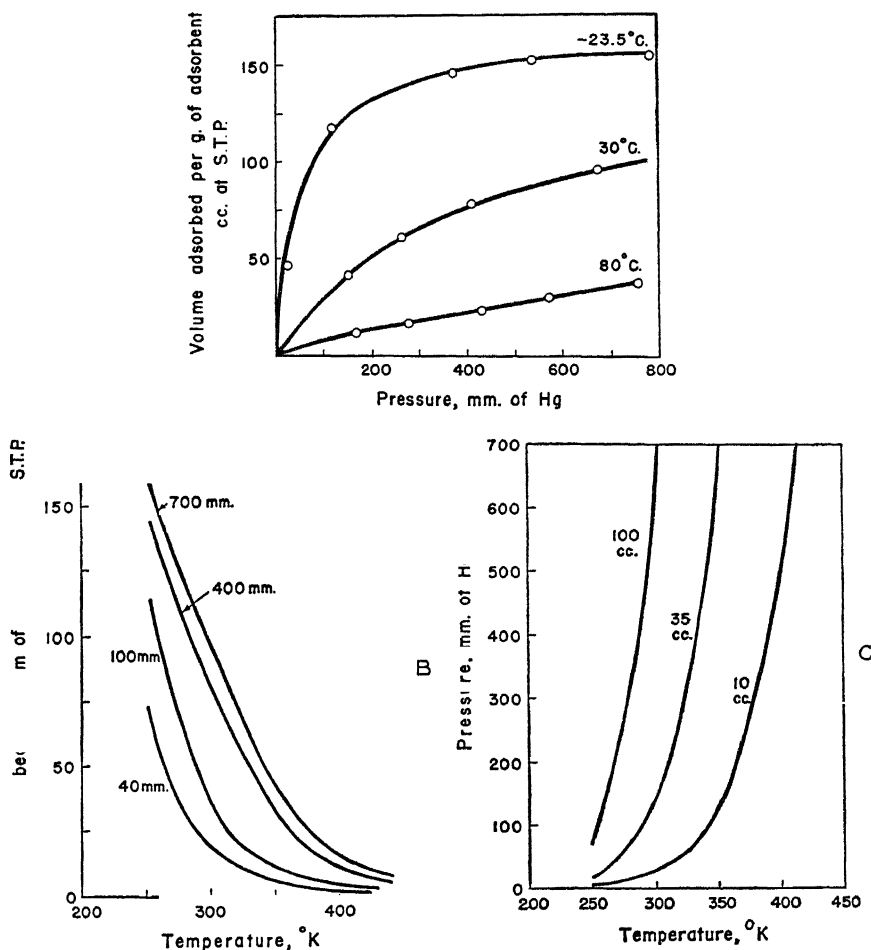


FIG. 26. Adsorption of Ammonia on Charcoal (A) Isotherms, (B) Isobars, and (C) Isosteres. (Adapted from Brunauer, *The Adsorption of Gases and Vapors*, Vol. I.)

of Le Chatelier, because the adsorption process is always exothermic. If the gas is adsorbed in two forms, however, e.g., van der Waals adsorption at low temperatures and chemisorption at higher temperatures, the adsorption first decreases with increasing temperature, due to decreasing van der Waals adsorp-

tion, and then begins to increase at temperatures where activated adsorption can take place.<sup>3</sup>

(43) **Adsorption Theories:** Since the earlier adsorption theories of Langmuir<sup>1</sup> and of Polanyi,<sup>2</sup> important advances have been made in the study of solid surfaces. The study of catalysts in particular has led to the extension of our knowledge concerning adsorption, and the development of theories has grown out of attempts to measure the surface area of porous and finely divided materials.

A number of attempts have been made to utilize chemisorption or physical adsorption measurements in estimating the surface areas of porous or finely divided solids. The use of chemisorption measurements for this purpose is

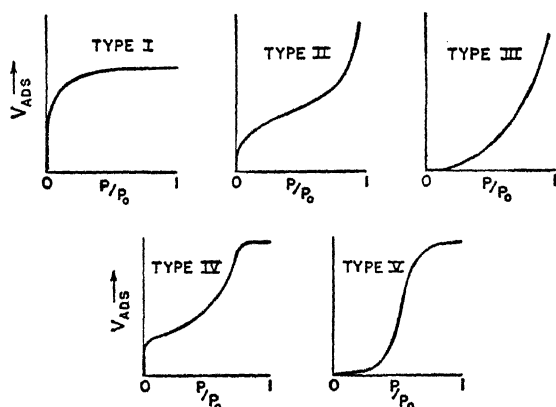


FIG. 27. Five Types of van der Waals Adsorption Isotherms. (Brunauer, Deming, Deming and Teller.)

limited because of the difficulty in finding a gas that will be chemically adsorbed over the entire surface. Physical adsorption, on the other hand, is more general and five different types of isotherms have been observed. The five types illustrated in Fig. 27 are exemplified by the adsorption of oxygen on charcoal at  $-183^{\circ}\text{C}$  (type I),<sup>3</sup> nitrogen on iron catalysts at  $-195^{\circ}\text{C}$  (type II),<sup>4</sup> bromine on silica gel at  $79^{\circ}\text{C}$  (type III),<sup>5</sup> benzene on ferric oxide gel at  $50^{\circ}\text{C}$  (type IV),<sup>6</sup> and water vapor on charcoal at  $100^{\circ}\text{C}$  (type V).<sup>7</sup> Langmuir<sup>8</sup> interpreted the

<sup>3</sup> Langmuir, *J. Am. Chem. Soc.*, **40**, 1361 (1918).

<sup>1</sup> Langmuir, *Phys. Rev.*, **8**, 149 (1916); *J. Am. Chem. Soc.*, **38**, 2221 (1916); **40**, 1361 (1918).

<sup>2</sup> Polanyi, *Verhandl. deut. physik. Ges.*, **16**, 1012 (1914); **18**, 55 (1916); *Z. Elektrochem.*, **26**, 370 (1920); **28**, 110 (1922).

<sup>3</sup> Brunauer and Emmett, *J. Am. Chem. Soc.*, **59**, 2682 (1937).

<sup>4</sup> *Ibid.*, 1553 (1937).

<sup>5</sup> Reyerson and Cameron, *J. Phys. Chem.*, **39**, 181 (1936).

<sup>6</sup> Coolidge, *J. Am. Chem. Soc.*, **49**, 708 (1927).

<sup>7</sup> Lambert and Clark, *Proc. Roy. Soc.*, **A122**, 497 (1929).

<sup>8</sup> *J. Am. Chem. Soc.*, **37**, 1139 (1915).

type I isotherm in terms of the kinetics of monolayer adsorption. Brunauer, Emmett and Teller<sup>9</sup> derived an isotherm equation for the multimolecular adsorption of gases that includes types I, II, and III. Brunauer, Deming, Deming and Teller<sup>10</sup> have extended the isotherm equation for van der Waals adsorption of gases to cover types IV and V. These theories are discussed briefly in the following sections.

(44) **Langmuir's Adsorption Theory:** Langmuir pictured the surface of a solid as a mosaic of elementary spaces having a certain small number of atoms in a particular arrangement; each kind of elementary space is the source of specific residual valence forces extending approximately  $10^{-8}$  cm from the surface. On the face of a crystalline element like the diamond, all elementary spaces are alike and the corresponding pattern of surface valence forces is uniform and simple.<sup>1</sup> In general, however, a crystal face has a number of different kinds of elementary spaces, each kind producing a regular lattice of surface forces; the surface fractions occupied by the different kinds of spaces are numerically related in a simple fashion. The surface of an amorphous body contains an indefinite number of kinds of elementary spaces and a correspondingly complicated surface-valence pattern. Adsorption consists in the chemical union of elementary spaces with molecules of the adjacent gas in a manner that depends upon the specific forces involved, the relative sizes of the elementary spaces and the adsorbed molecules, and the orientation of the latter. Owing to the short range of the surface-valence forces, but a single layer of molecules can normally be adsorbed. In an ordinary case the combination is reversible, adsorbed molecules re-evaporating and gas molecules condensing on the surface, much as they do at the surface of a liquid and its vapor.

The application of these ideas may be illustrated by the simplest case, in which all elementary spaces are alike and each one may adsorb one molecule of gas, i.e., if the adsorbent contains  $N_0$  spaces per square centimeter, the maximum possible adsorption is  $N_0$  molecules or  $N_0/N$  moles per square centimeter,  $N$  being the Avogadro number. At adsorption equilibrium the rate of evaporation of the adsorbed gas in moles per square centimeter per second is  $\theta\nu$ , where  $\nu$  is the rate when all elementary spaces are occupied and  $\theta$  is the fraction actually occupied. The corresponding rate of condensation of gas molecules on the surface is  $\alpha(1 - \theta)\mu$ , where  $\mu$  is the rate with which gas molecules strike the surface in moles per square centimeter per second,  $(1 - \theta)$  is the uncovered fraction of the surface, and  $\alpha$  is the fraction of molecules striking unoccupied spaces which condenses. Equating the two opposing rates, solving for  $\theta$ , and substituting  $\sigma$  for the ratio  $\alpha/N$ , gives the adsorption as a

<sup>9</sup> *Ibid.*, 60, 309 (1938).

<sup>10</sup> *Ibid.*, 62, 1723 (1940).

<sup>1</sup> By means of electron diffraction from crystal surfaces carrying an adsorbed gas, Davisson and Germer (*Phys. Rev.*, 30, 705 [1927]; also Germer, *Z. Physik*, 54, 408 [1929]) have provided strong evidence for the view that the adsorbed gas in an ideal case possesses a characteristic pattern that is determined by the pattern formed by the surface atoms of the solid adsorbent. See also Rupp, *Z. Elektrochem.*, 35, 586 (1929).



fraction of the maximum; thus,  $\theta = \sigma\mu(1 + \sigma\mu)$ , where  $\sigma$  is proportional to the average life of a molecule in the adsorbed condition, and  $\mu$  is by kinetic theory proportional to the gas pressure, i.e.,  $\mu = p/\sqrt{2\pi MRT}$ ,  $M$  being the molecular weight of the gas. The adsorption  $\Gamma$  in moles per square centimeter is therefore equal to  $N_0/N$  multiplied by  $\theta$ ; thus,

$$\Gamma = \frac{N_0}{N} \left( \frac{\sigma\mu}{1 + \sigma\mu} \right) = \frac{N_0}{N} \left( \frac{\sigma p}{\sqrt{2\pi MRT} + \sigma p} \right) \quad (44.1)$$

which represents a curve starting from the origin with the slope  $N_0\sigma/N\sqrt{2\pi MRT}$  and gradually approaching the maximum  $N_0/N$ . Inasmuch as the constants  $N_0$  and  $\sigma$  must be empirically determined from the adsorption isotherm, and the area of the adsorbent per gram is usually unknown, the simpler form of the equation,  $a = kp/(1 + bp)$  (see p. 603), is more convenient and just as useful when it is simply desired to describe an adsorption isotherm mathematically.

(45) **BET Theory:** Brunauer, Emmett and Teller<sup>1</sup> (BET) postulated the building up of multimolecular adsorption layers on the catalyst surface, and extended Langmuir's derivation for single molecular layers to obtain an isothermal equation for multimolecular adsorption.<sup>2</sup> At equilibrium the rate of condensation of molecules to form a certain layer is equal to the rate of escape of molecules from that layer, so that if  $s_0, s_1, s_2, \dots, s_i$  represent the areas of the adsorbent covered by 0, 1, 2,  $\dots, i$  layers of adsorbate and  $E_1, E_2, \dots, E_i$  are the average heats of adsorption of the gas in the first, second,  $\dots, i$ th layers, respectively, application of the principle of microscopic reversibility yields

$$a_1 p s_0 = b_1 s_1 e^{-E_1/RT} \quad (45.1)$$

$$a_2 p s_1 = b_2 s_2 e^{-E_2/RT} \quad (45.2)$$

$$a_3 p s_2 = b_3 s_3 e^{-E_3/RT} \quad (45.3)$$

where  $a$  and  $b$  are constants and  $p$  is the pressure. The total surface area of the catalyst is

$$A = \sum_{i=0}^{\infty} s_i \quad (45.4)$$

and the total volume adsorbed is

$$V = V_0 \sum_{i=0}^{\infty} i s_i \quad (45.5)$$

<sup>1</sup> *J. Am. Chem. Soc.*, **60**, 309 (1938).

<sup>2</sup> The BET equation has more recently been derived by Cassie, *Trans. Faraday Soc.*, **41**, 450 (1945); Hill, *J. Chem. Phys.*, **14**, 263 (1946); and Dole, *ibid.*, **16**, 25 (1948), by a statistical thermodynamic approach. More recently the fundamental postulates of the theory have been subjected to certain criticism and it appears that important modifications are imminent. Cf. Halsey, *J. Chem. Phys.*, **17**, 753 (1949); Hill, *ibid.*, **17**, 106 (1949).

where  $V_0$  is the volume of gas adsorbed on one  $\text{cm}^2$  of the adsorbent surface when it is covered with a complete unimolecular layer of adsorbed gas. The volume  $V_m$  of gas adsorbed when the entire adsorbent surface is covered with a complete monomolecular layer is

$$V_m = AV_0 = V \sum_{i=0}^{\infty} s_i \quad (45.6)$$

The summation may be carried out if we make the simplifying assumption that  $E_2 = E_3 = \dots E_i = E_L$ , where  $E_L$  is the heat of liquefaction for the gas and,

$$\overline{a_2} = \overline{a_3} = \dots = \overline{a_i} = g$$

$g$  being a constant.

The following equation is obtained if the summation of the multimolecular layers is limited to layers  $n$  molecules thick,

$$V = \frac{V_m c x [1 - (n+1)x^n + nx^{n+1}]}{(1-x)[1 + (c-1)x - cx^{n+1}]} \quad (45.7)$$

$x$  being equal to  $p/p_0$ , where  $p_0$  is the saturation pressure of the gas, and  $c$  is approximately  $e^{(E_1 - E_L)/RT}$ .

If  $n = 1$ , Equation (45.7) reduces to the Langmuir equation of the form

$$\frac{p}{V} = \frac{p_0}{cV_m} + \frac{p}{V_m} \quad (45.8)$$

Since the manner in which  $p_0$  and  $c$  change with temperature is known, it thus becomes possible to use the Langmuir equation in this form to calculate isotherms at one temperature from those at another.

If  $n = \infty$  (free surface) or for  $p/p_0$  values smaller than about 0.4 and  $n > 4$ , Equation (45.7) becomes

$$\frac{p}{V(p_0 - p)} = \frac{1}{V_m c} + \frac{(c-1)p}{V_m c p_0} \quad (45.9)$$

According to this equation a plot of  $p/V(p_0 - p)$  vs.  $p/p_0$  should give a straight line whose slope is  $(c-1)/V_m c$  and whose intercept is  $1/V_m c$ . Thus from the slope and intercept, the volume of gas required to form a complete monomolecular adsorbed layer may be determined. Typical plots of Equation (45.9) for the adsorption of nitrogen at 90.1°K on a variety of adsorbents for which S-shaped isotherms have been obtained are given in Fig. 28. Between the relative pressures  $p/p_0$  of 0.05 and 0.35 the plots are closely linear. The  $V_m$  and  $E_1 - E_2$  values obtained from these plots are recorded in Table XVI. After the value of  $V_m$  is obtained from the isotherm, multiplication of the number of molecules required to form a monomolecular layer by the average

area occupied by each molecule on the surface gives the absolute value of the surface area of the adsorbent. The surface area occupied by an adsorbed molecule on the surface may be calculated from the density of the liquefied or solidified adsorbate. If the physically adsorbed molecules are close-packed on the surface, the average area per molecule is given by

$$A = 4(0.866) \left( \frac{M}{4\sqrt{2} N \rho} \right)^2 \quad (45.10)$$

where  $M$  is the molecular weight of the gas,  $N$  is Avogadro's number and  $\rho$  is the density of the solidified or liquefied gas. The areas calculated from the density of the solid (S) and the density of the liquid (L) for a number of different gas molecules are given in Table XVII. In Table XVI the surface area in square meters per gram ( $\text{m}^2/\text{g}$ ) has been calculated from the isotherms of different gases adsorbed on silica gel using the cross-sectional areas of the adsorbed molecules derived from both the density of the solidified gas and of the liquefied gas. The surface areas per gram

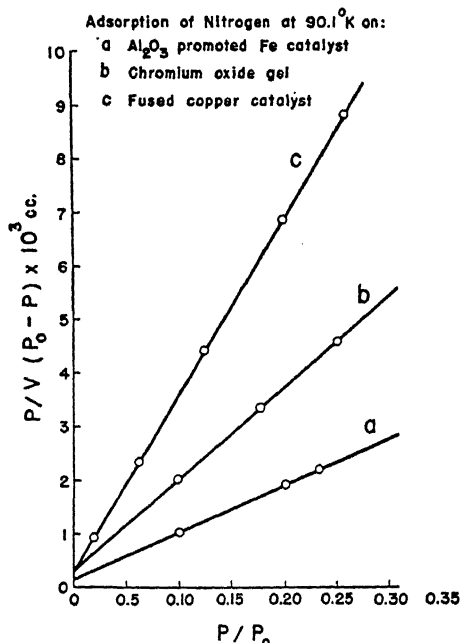


FIG. 28. BET Plots for the Adsorption of Nitrogen at 90.1°K. (Brunauer, Emmett, and Teller.)

of silica gel calculated from one gas agree approximately with those calculated from another gas.

The theory of the van der Waals adsorption of gases has been extended<sup>3</sup> to include the region with  $p/p_0$  values lying between 0.35 and 1 for S-shaped isotherms and to include the remaining types given in Fig. 27. Type III isotherms are typical of systems in which the forces between adsorbent and adsorbate are small and may be described by Equation (45.7) by putting  $E_1 = E_L$ . Types IV and V suggest that the complete or almost complete filling of the pores and capillaries of the adsorbent occurs at a pressure lower than the vapor pressure of the gas. To explain such isotherms for the special case in which the capillaries are assumed to be bounded by plane parallel walls, a detailed statistical analysis was made, taking into account the fact that the last layer of molecules going into a crack will be attracted by the multimolecular layer on both walls and hence will have a heat of adsorption that is  $Q$  cal. higher

<sup>3</sup> Brunauer, Deming, Deming and Teller, *J. Am. Chem. Soc.*, **62**, 1723 (1940).

TABLE XVI  
 VALUES OF CONSTANTS FOR ADSORPTION ISOTHERMS ON SILICA GEL

Gas	Temp., °C	$V_m$ , cc/g	Surface, m <sup>2</sup> g <sup>-1</sup>		$E_1 - E_2$ , cal/mole
			Solid packing	Liquid packing	
N <sub>2</sub> .....	-196	127.9	477	560	719
N <sub>2</sub> .....	-183	116.2	434	534	794
A.....	-183	119.3	413	464	594
O <sub>2</sub> .....	-183	125.1	410	477	586
CO.....	-183	121.2	449	550	973
CO <sub>2</sub> .....	-78	99.0	378	455	1335
C <sub>4</sub> H <sub>10</sub> .....	0	58.2	504	504	1930

than that of the next lower layers. This theory, however, does not deal with the hysteresis that characterizes the desorption of gases from many porous solids and which is described in Section 48.

 TABLE XVII<sup>1</sup>  
 AREA OCCUPIED BY EACH ADSORBED MOLECULE

	Area (S) Å <sup>2</sup>	Area (L) Å <sup>2</sup>
N <sub>2</sub> .....	13.8	17.0 (-183°) 16.2 (-195°)
O <sub>2</sub> .....	12.1	14.1
A.....	12.8	14.4
CO.....	13.7	16.8
CO <sub>2</sub> .....	14.1	17.0
C <sub>4</sub> H <sub>10</sub> .....	32.0	32.1

<sup>1</sup> Emmett and Brunauer, *J. Am. Chem. Soc.*, 59, 1553 (1937).

(46) **Absolute Method for the Determination of the Area of a Finely Divided Crystalline Solid:** The method which was developed by Harkins and Jura,<sup>1</sup> does not depend on a knowledge of the area occupied by the adsorbed molecules, but upon accurate calorimetric measurements. A finely divided crystalline solid is suspended in the saturated vapor of a liquid until it becomes coated with an adsorbed film. If this liquid gives a zero angle of contact with the solid, the adsorbed film thickens, until at equilibrium its surface energy becomes the same as that of the liquid in bulk. The system is allowed to come into thermal equilibrium in a sensitive calorimeter as illustrated in Fig. 29 and then the crystals are dropped into the liquid. The only energy change involved

<sup>1</sup> *J. Am. Chem. Soc.*, 66, 1362 (1944); *J. Chem. Phys.*, 11, 430 (1943).

is that due to the disappearance of the liquid surface of the adsorbed film. If the liquid has a total surface energy of  $h_L$  at the temperature of the experiment, the outer area of the film ( $\Sigma'$ ) is given by the relation

$$\frac{H_E}{h_L} \quad (46.1)$$

where  $H_E$  is the heat of immersion of the film-covered powder. To obtain the area of the uncoated particle it is necessary to make a small correction for the

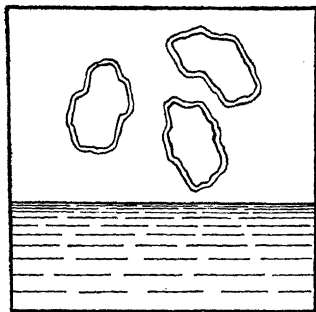


FIG. 29. Crystals in equilibrium with the Vapor of a Liquid: to be immersed in the liquid and thus lose the surface energy of the duplex film of liquid.

thickness of the adsorbed film. The mass of the adsorbed film may be determined by weighing, and the mean equivalent thickness may be calculated from the density of the liquid. This method is applicable only to nonporous solids, and extremely difficult calorimetric measurements are required unless the particles are quite fine. The area of a sample of anatase ( $\text{TiO}_2$ ) was found to be  $13.8 \text{ m}^2/\text{g}$  by this method, while the BET method gave  $13.9 \text{ m}^2/\text{g}$  by the use of the usual assumption of  $16.2 \text{ \AA}^2$  as the area per nitrogen molecule (calculated from the density of liquid nitrogen) in the complete monolayer.

**(47) Relative Method for the Determination of the Area of a Porous or Nonporous Solid:** This method, developed by Harkins and

Jura<sup>1</sup> (HJ), is a vapor-adsorption method which is independent of the area of the adsorbed molecules and is also applicable to porous solids. Since it is only a relative method, a constant must be determined for each adsorbate by the absolute method. Jura and Harkins<sup>2</sup> have found that the pressure ( $\pi$ )-area ( $\sigma$ ) relations for condensed films on solids may be represented by

$$b - a\sigma \quad (47.1)$$

where  $a$  and  $b$  are constants. This may be transformed to the equivalent relation

$$\log \left( \frac{p}{\pi} \right) = B - \frac{S \cdot}{\pi^2} \quad (47.2)$$

where  $V$  is the amount of vapor adsorbed, and  $B$  and  $S$  are constants. This isothermal relationship is valid over more than twice the pressure range of any other two-constant adsorption isotherm. It was found that the area of the solid is proportional to the square-root of the slope of this plot so that

$$kS^{1/2} \quad (47.3)$$

<sup>1</sup> *J. Chem. Phys.*, **11**, 431 (1943); *J. Am. Chem. Soc.*, **66**, 1366 (1944).

<sup>2</sup> *J. Chem. Phys.*, **11**, 430 (1943).

By determining  $S$  for a powder of known area, the constant  $k$  may be evaluated. The agreement with the BET method (using  $16.2 \text{ \AA}^2$  for the area of a nitrogen molecule) is very satisfactory as may be seen from the following table of areas calculated from nitrogen adsorption isotherms at  $-195.8^\circ\text{C}$ .

TABLE XVIII

Crystalline solid	Surface area, $\text{m}^2/\text{g}$	
	HJ	BET
$\text{TiO}_2$ .....	13.8	13.9
$\text{TiO}_2 + \text{Al}_2\text{O}_3$ .....	9.6	9.5
$\text{ZrSiO}_4$ .....	2.9	2.8
$\text{BaSO}_4$ .....	2.4	2.4
$\text{SiO}_2$ (Quartz).....	3.2	3.2

Phase changes in the region of the isotherm used to determine the surface area may interfere with the application of Equation (47.2). No phase change has been described so far for adsorbed nitrogen over the range of 0.05 to about 0.3 for  $p/p_0$  usually employed for BET plots. The significance, usefulness and limitations of the various multilayer adsorption equations has been reviewed by Emmett.<sup>3</sup>

(48) **Capillary Condensation and Hysteresis:** If the adsorbent is porous on a submicroscopic scale, so-called capillary condensation occurs below the normal saturation pressure, for as Thomson (Lord Kelvin),<sup>1</sup> showed, the saturation pressure ( $p$ ) over a concave liquid surface is lower than over a large plane surface ( $p_s$ ). Upon the assumption that the surface tension does not change with curvature and the vapor obeys the ideal gas laws,

$$\ln \frac{p}{p_s} = - \frac{2\gamma V}{rRT} \quad (48.1)$$

where  $\gamma$  is the surface tension,  $V$  is the molar volume, and  $r$  the radius of curvature. This equation is usually known as the Kelvin equation. The change in vapor pressure is appreciable only for very small capillaries, in which case there is some question as to the exactness of the equation;<sup>2</sup> for water at room temperature a theoretical decrease in vapor pressure of approximately one per cent occurs in capillaries of  $10^{-5} \text{ cm}$ . During adsorption, therefore, condensation takes place in the smaller capillaries at a lower pressure than in the larger

<sup>3</sup> *J. Am. Chem. Soc.*, **68**, 1784 (1946).

<sup>1</sup> Thomson (Lord Kelvin), *Phil. Mag.*, **42**, 448 (1881).

\* The same relation, with a change in the sign of  $r$ , is applicable to convex surfaces where the vapor pressure is greater than at a plane surface, and also to the increased solubility of small particles,  $p/p_s$  being replaced by the ratio of solubilities.

<sup>2</sup> Experiments of Shereshevsky, *J. Am. Chem. Soc.*, **50**, 2966, (1928), indicate that the vapor pressure lowering is greater than predicted by the Kelvin equation.

one. Cohan<sup>3</sup> has shown that in the case of capillaries open at both ends the walls become covered with a thin film of liquid, but condensation will not take place until  $p_r$  is reached and at that pressure, which is given by

$$\ln \frac{p_r}{p_s} = - \frac{\gamma V}{rRT} \quad (48.2)$$

where  $r$  is the radius of the cylindrical film in the capillary, the capillary fills completely since  $p_r$ , the vapor pressure of the outermost annular ring, is greater than that of any ring farther away from the walls. It will be noted that Equation (48.2) differs from the Kelvin equation by a factor of 2. The pressure range in which the adsorption increases very rapidly, therefore, yields information as to the size and size distribution of the pores. Upon desorption the  $V$  vs.  $p/p_0$  curve for porous materials frequently does not follow the same path and in all cases the adsorption is apparently greater when equilibrium is approached from higher pressures than from lower pressures. This hysteresis effect may be reversible, that is, upon repetition of the experiment the adsorption isotherm is completely reproduced, or the hysteresis may be irreversible. Zsigmondy's<sup>4</sup> explanation of irreversible hysteresis in terms of the capillary condensation theory is that during adsorption the vapor does not wet the wall of the adsorbent completely because of impurities, such as air, adsorbed on the walls of the capillary pores so that the contact angle is not zero. The pressures  $p$  corresponding to capillary condensation would therefore be given by

$$\ln \frac{p}{p_s} = \frac{-2\gamma V \cos \theta}{rRT} \quad (48.3)$$

where  $\theta$  is the contact angle. During desorption, when the contact angle is zero, the equilibrium pressures are given by the usual form of the Kelvin equation and are less than those during adsorption so that evaporation from the capillaries does not take place until lower pressures are reached. Patrick<sup>5</sup> found, as the theory would predict, that drastic evacuation removed the irreversible hysteresis in the adsorption of water by a sample of silica gel. Although there is no doubt about the existence of irreversible hysteresis, Pigeon<sup>6</sup> pointed out that in the experiments reported by Patrick a large volume of silica gel was examined in a relatively small apparatus and that this procedure might result in tracing simultaneously the sorption and desorption curves regardless of whether the gel was decreasing or increasing in water content. For this reason it is necessary to take care to add or remove exceedingly small increments or decrements of vapor during adsorption and desorption in order that the successive points on the curves be obtained under substantially isobaric conditions.

<sup>3</sup> *J. Am. Chem. Soc.*, **60**, 433 (1938).

<sup>4</sup> *Z. anorg. Chem.*, **71**, 356 (1911).

<sup>5</sup> *Colloid Symposium Annual*, 1930, p. 129.

<sup>6</sup> *Can. J. Research*, **10**, 713 (1934).

Frequently hysteresis is reversible. Such behavior may be explained in terms of the "ink bottle" theory which was suggested by Kraemer<sup>7</sup> and elaborated by McBain,<sup>8</sup> and by the open-pore theory suggested by Foster<sup>9</sup> and given quantitative consideration by Cohan.<sup>10</sup> If the pores in the adsorbent are shaped like ink bottles, having narrow necks and wide bodies, the narrow neck will fill at relatively low pressures on the adsorption side, but condensation in the body, where the radius of the capillary is greater, will take place only at higher pressures. On desorption, evaporation cannot take place in the body

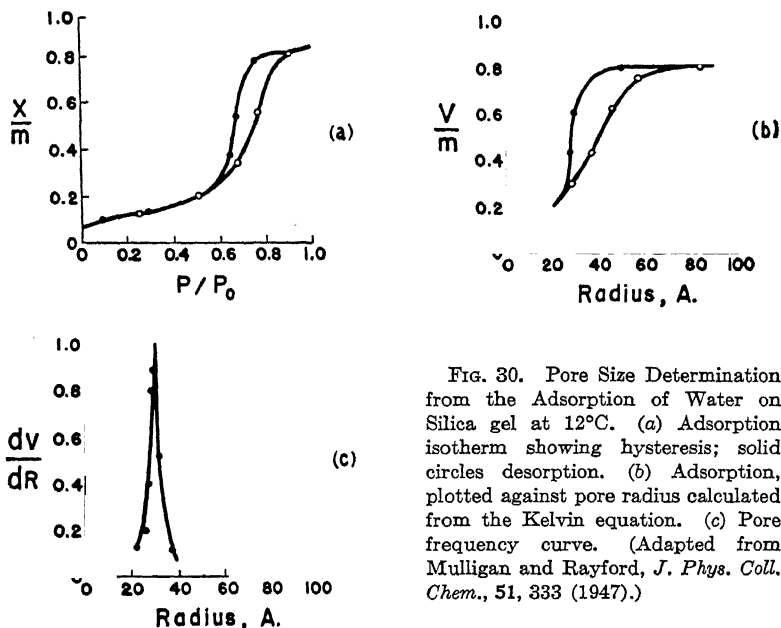


FIG. 30. Pore Size Determination from the Adsorption of Water on Silica gel at 12°C. (a) Adsorption isotherm showing hysteresis; solid circles desorption. (b) Adsorption, plotted against pore radius calculated from the Kelvin equation. (c) Pore frequency curve. (Adapted from Mulligan and Rayford, *J. Phys. Coll. Chem.*, 51, 333 (1947).)

of the pore until the pressure has been reduced so far that the liquid in the narrow neck of the pore evaporates. According to this picture, the wider the hysteresis loop, the greater the difference between the radius of the body of the average pore and the radius of its capillary neck. Hysteresis in pores open at both ends results from the fact that in desorption, evaporation must be from a meniscus for which the relation between vapor pressure and radius is given by the Kelvin equation (48.1), while in adsorption the minimum pressure at which the capillaries fill is given by Cohan's equation (48.2). It is evident from these equations that for a cylindrical capillary of given radius, the partial

<sup>7</sup> Kraemer, in Taylor, *A Treatise on Physical Chemistry* (2d ed.; New York: D. Van Nostrand Co., Inc., 1930). Vol. II, p. 1661.

<sup>8</sup> McBain, *J. Am. Chem. Soc.*, 57, 699 (1935).

<sup>9</sup> Trans. *Faraday Soc.*, 28, 645 (1932).

<sup>10</sup> *Loc. cit.*



pressure of desorption should be equal to the square of the adsorption pressure. Emmett<sup>11</sup> found that such a relationship existed for the adsorption and desorption curves for nitrogen on porous glass.

Foster<sup>12</sup> obtained the structure curves of ferric oxide gel and silica gel by plotting the capillary radius corresponding to a given  $p/p_s$  calculated from the Kelvin equation, against the volume of liquid adsorbed. Figure 30a shows such a curve for the adsorption of water on silica gel at 12°C. This curve gives the volume of liquid necessary to fill all the pores having radii equal to or less than  $r$ . An addition of a small amount of liquid  $dv$  fills up the pores having radii between  $r$  and  $r + dr$ , so that the curve obtained (Fig. 30c) by plotting  $dv/dr$  against  $r$  shows the contribution of the pores of radius  $r$  to the total capillary volume of the gel. The peak of such a pore-frequency curve corresponds to the point of inflection on the desorption branch and gives the radius of the most frequently occurring capillary in the gel.

(49) **Heat of Adsorption:**<sup>1</sup> Adsorption from gases or solutions is generally exothermic in agreement with Le Chatelier's principle and the negative temperature coefficient of adsorption. Heats of adsorption from solution, like amounts of adsorption, are complicated by the participation of the solvent and are correspondingly difficult to interpret.<sup>2</sup>

In gaseous adsorption, the heat change is an important quantity in the thermodynamic analysis of the process. The "total" or "integral" heat of adsorption is the heat change accompanying the isothermal adsorption of a specified quantity of gas, beginning with a gas-free adsorbent; it has been studied with both isothermal and adiabatic calorimeters. The "differential" heat of adsorption is the heat given off when one mole of gas is adsorbed by a very large quantity of adsorbent already laden with a specified amount of gas. The isosteres shown in Fig. 27 resemble vapor pressure curves because every point represents a pressure and temperature at which the adsorbent laden with a specified amount of gas is in equilibrium with the vapor. The Hückel equation may be used to calculate the isosteric heat of adsorption,  $q$ ; thus,

$$\frac{d \ln p}{d(1/T)} = \frac{-q}{R} \quad (49.1)$$

According to this equation, plotting the isosteric data as  $\ln p$  vs.  $1/T$  should give straight lines. The decrease in the differential heat of adsorption, as calculated from Equation (49.1), with increasing adsorption indicates a non-uniformity of the surface of the adsorbent.<sup>3</sup>

<sup>11</sup> Emmett, in Kraemer, *Advances in Colloid Science* (1942), Vol. 1.

<sup>12</sup> Foster, *loc. cit.*

<sup>1</sup> Brunauer, *The Adsorption of Gases and Vapors*, Princeton: Princeton Univ. Press (1943), Vol. I.

<sup>2</sup> See Bartell and Fu, *J. Phys. Chem.*, **33**, 1758 (1929), for an interesting treatment of such cases.

<sup>3</sup> Taylor, *J. Phys. Chem.*, **30**, 145 (1926); *Proc. Roy. Soc.*, A108, 105 (1925).

When the quantity of gas admitted is insufficient to cover the entire surface, at first the most active part of the surface adsorbs gas, and the heat of adsorption is the largest. However, owing to the divariant character of adsorption equilibrium, several differential heats must be recognized: e.g., the isosteric heat of adsorption, corresponding to a heat of evaporation and related to the temperature coefficient of the equilibrium gas density with a constant amount of adsorbed gas; and the isobaric heat, corresponding to a heat of reaction in a condensed system and related to the temperature coefficient of the amount adsorbed at constant pressure.

Titoff <sup>4</sup> found a reasonably good agreement between heats of adsorption of nitrogen, carbon dioxide and ammonia on charcoal, and values calculated from the temperature coefficients of adsorption.

Lamb and Coolidge <sup>5</sup> found that the variation in heat of adsorption with the amount of gas adsorbed followed the empirical formula

$$q = ma^n$$

where  $q$  is the total heat evolved when the amount of gas adsorbed is  $a$  cm<sup>3</sup>/g (integral heat of adsorption) and  $m$  and  $n$  are constants. The value of  $n$  is near unity in all cases, ranging from 0.900 for ethyl bromide to 0.959 for benzene. The molar heats of adsorption, for an adsorption of one mole of vapor by 500 g of charcoal, increase in the order: ethyl chloride (12,000 cal/mole) < carbon disulfide < methyl alcohol < ethyl bromide < ethyl iodide < chloroform < ethyl formate < benzene < ethyl alcohol < carbon tetrachloride < acetone (15,500 cal/mole). Lamb and Coolidge found that the ratio of the difference between the molar heat of adsorption and the molar heat of liquefaction to the molar volume of the liquid adsorbed was 38 cal/cm<sup>3</sup> of liquid for all of the above liquids with an average error of 7.4 per cent. It was concluded that the adsorbed substance is condensed to a liquid film and compressed by an attractive force of 37,000 atm. Keyes and Marshall <sup>6</sup> obtained values for the molar differential heats of adsorption of various gases and vapors on charcoal at high equilibrium pressures, which were approximately 10 to 20 per cent greater than the energy theoretically liberated, on account of cohesive forces, upon compressing one mole of gas from an infinitely dilute condition to the "minimum" volume. The differential heats of adsorption for the first stages of adsorption were many times greater for oxygen and chlorine, over twice as great for ammonia and ethyl ether, and about 10 per cent and 50 per cent greater for water and carbon dioxide, respectively. The heats of adsorption for gases on catalytically active metals (H<sub>2</sub>, CO on Pt, Ni, Cu) also are often much greater than the heats of liquefaction and vary widely for different samples of the adsorbent or at different stages of adsorption. These heat changes throw considerable light upon the question of catalytic activity.

<sup>4</sup> *Z. physik. Chem.*, **74**, 641 (1910).

<sup>5</sup> Lamb and Coolidge, *J. Am. Chem. Soc.*, **42**, 1146 (1920).

<sup>6</sup> *Ibid.*, **49**, 156 (1927).

In an interesting group of papers, Hill <sup>7</sup> has clarified the whole subject of heats of adsorption.

(50) **Wetting of Solid Surfaces:** The usual methods for measuring adsorption from gases or solutions fail for pure liquids because no change in bulk concentration can take place, and the pressure or volume change, in comparison to that for gaseous adsorption, is practically nil.<sup>1</sup> Since the vapor of a liquid is condensed at the surface of a solid, it seems reasonable to suppose that the surface forces also tend to condense the liquid itself; in any case the properties of a pure liquid are usually modified at an interface with a solid. To emphasize the relation between these effects and those occurring with gases or solutions, the liquid is said to be "adsorbed" by the solid even though there may be no appreciable increase in concentration at the interface.

One manifestation of the mutual interaction of a solid and a liquid at an interface is revealed by a heat of wetting, which, in the absence of solubility and other complications, is in fact the integral heat of adsorption for the saturated vapor plus the total surface energy of the liquid for an area equal to that of the solid interface.<sup>2</sup> The determination of the heat of immersion has been highly developed both from the technical and theoretical points of view. Harkins <sup>3</sup> shows that with data from simple auxiliary experiments, the heat of immersion can be used to give (1) the energy required to separate a solid from a liquid (energy of adhesion); (2) the integral and differential heats of adsorption; (3) the decrease in total surface energy caused by the adsorption of a vapor or liquid on the surface of the solid; (4) the true area of the solid; and (5) the free energy change at any temperature, when it is known at one temperature.

Another manifestation of the mutual interaction of a solid and liquid at an interface is the "contact angle." This is the angle, equal to or greater than zero, at the line of contact between the solid and the liquid as measured in the liquid phase. This angle may be measured by photographing the meniscus <sup>4</sup> or by the use of a tilting plate,<sup>5</sup> or vertical rod.<sup>6</sup> According to the classical theory of capillarity, the contact angle  $\theta$  is related to the three interfacial ten-

<sup>7</sup> Hill, *J. Chem. Phys.*, **17**, 507, 520 (1949).

<sup>1</sup> The considerable apparent expansion that occurs with porous bodies like charcoal (Harkins and Ewing, *J. Am. Chem. Soc.*, **43**, 1787 [1921]) probably is due to imperfect penetration of the liquid into the pores (Howard and Hulett, *J. Phys. Chem.*, **28**, 1082 [1924]). A definite contraction, however, can be measured for dry gelatin, rubber, and the like, when they are immersed in a liquid causing swelling (see Posnjak, *Kolloidchem. Beih.*, **3**, 431 (1912); Katz, *ibid.*, **9**, 70 (1917); Svedberg, *Colloid Chemistry* (2d ed.; 1928), p. 215).

<sup>2</sup> See review of data on heats of wetting by Browne and Mathews, in Alexander, *Colloid Chemistry*, Vol. I, chap. 25.

<sup>3</sup> Harkins, in Alexander, *Colloid Chemistry*, Vol. VI, chap. I.

<sup>4</sup> Richards and Carver, *J. Am. Chem. Soc.*, **43**, 827 (1921) found the contact angle between water and glass to be zero by this method.

<sup>5</sup> Adam and Jessop, *J. Chem. Soc.*, 1865 (1925); Harkins and Fowkes, *J. Am. Chem. Soc.*, **62**, 3377 (1940).

<sup>6</sup> Bartell, Culbertson, and Miller, *J. Phys. Chem.*, **40**, 881 (1936).

sions involved by the equation

$$\cos \theta = \frac{\gamma_{S-G} - \gamma_{S-L}}{\gamma_{L-G}} \quad (50.1)$$

where  $S$ ,  $L$ , and  $G$  refer to the solid, liquid, and gas phases in equilibrium with each other, and  $\gamma_{S-G} - \gamma_{S-L}$  is the "adhesion tension," which may be considered as a measure of the relative wetting tendency.<sup>7</sup> The adhesion tension is also theoretically related to the free adhesion energy and the spreading coefficient (cf. Equations (25.4) and (36.1)). Data in the literature show that contact angles formed with water drops on paraffin and on other soft hydrophobic solids have been readily reproducible on different samples of the same solid, while contact angles formed with water on relatively hard solids have not been readily reproducible when different samples of the same solid were used. The surface free energies of soft solids are low and adsorption effects must be low likewise. In contrast, the surface tensions of hard solids are relatively high, adsorption readily occurs and the clean surface of a pure solid may quickly become highly contaminated and thus altered in properties. Thus numerous investigators found that the contact angle was not definite for a given system, and that the contact angle formed when a liquid was caused to advance over a solid was greater than the angle formed when the liquid was caused to recede. Bartell<sup>8</sup> and coworkers have gone to extreme limits to eliminate contamination and to develop methods of preparing hard solid surfaces with reproducible properties, so that the problem of hysteresis of contact angles could be studied. In the case of the silver-air-water interface reproducible contact values for both advancing (95°) and receding (37°) angles were found. The 37° angle appears to be an equilibrium angle for water on fresh and uncontaminated silver while the 95° angle was the angle always obtained when the silver surface had been exposed to air for a relatively long time so that maximum air had become adsorbed upon it.

As mentioned on p. 571, the simple capillary-rise equation may be applied only to cases for which the contact angle is zero. In general the pressure in equilibrium with surface tension (for very small capillaries) is  $(2\gamma/R) \cos \theta$ . The contact angle, therefore, can theoretically be measured by capillary methods, provided the surface tension can be determined in some way that does not involve the contact angle. The adhesion tension then follows from Equation (50.1). Even if the liquid||air contact angle is zero, the adhesion tension can be determined by replacing the air with a liquid of known adhesion tension which is immiscible with the liquid to be studied and gives a contact angle greater than zero for the liquid||liquid interface. This angle is determined in the way just described for a solid-liquid-gas system,  $\gamma$  being the interfacial

<sup>7</sup> Freundlich, *Colloid and Capillary Chemistry*, p. 157; Bartell and Osterhof, *Fifth Colloid Symposium* (1927), p. 113; Bartell and Fu, *Seventh Colloid Symposium* (1929), p. 135; Bartell and Osterhof, *J. Phys. Chem.*, **37**, 543 (1933).

<sup>8</sup> Bartell and Cardwell, *J. Am. Chem. Soc.*, **64**, 494, 1530 (1942); Smith, *Thesis* (Michigan: 1944); Ray, *Thesis* (Michigan: 1945).

tension; Equation (50.1) then gives the difference between the two solid||liquid adhesion tensions, from which the unknown one is calculable.

Assuming that the pore system of a compressed powder is equivalent to a parallel group of uniform capillaries, Bartell and Osterhof<sup>9</sup> have applied these principles to the determination of contact-angles and adhesion tensions for a variety of solids and liquids. From the theory of capillary action it may be concluded that a liquid will not pass through such fine capillary pores unless it first wets the pore walls, but that, if the liquid does wet the pore walls, it will travel through the pores and so-called capillary action will occur. In case two liquid columns are in contact within such pores, other factors being equal, that liquid giving the higher interfacial tension against the solid will be displaced by the other liquid. Experimentally, the maximum pressures necessary to prevent any advance of the liquid||liquid interfaces within the pores of the powders were measured. The equivalent capillary radius of a given powder was determined by similar methods, using a liquid shown in some other way to have a zero contact angle. This unique method offers the only direct way to measure the true wetting characteristics of powders and porous solids. It has found application in studying the characteristics of powders, paint pigments, and of petroleum reservoir structures. It was found that the order of a series of liquids showing increasing adhesion tension values against silica is just the reverse of the order showing increasing adhesion values against carbon. Liquids giving the highest adhesion tension values against silica give the lowest adhesion tension values against carbon and vice versa. Presumably, the polar part of a molecule is oriented toward the silica and away from carbon, corresponding to a positive adsorption of the polar group in the first case and a negative adsorption in the second.

A number of important conclusions concerning solid||pure-liquid adsorption have been reached by Hardy<sup>10</sup> in a series of investigations of the static-friction coefficient for several solids and a large number of "lubricating" liquids. Static friction, e.g., due to slipping of a spherical slider on a plane surface, is due to molecular adhesion, i.e., solid||solid adsorption. Certain "lubricating" liquids reduce the adhesion and the static friction by forming a stable, semi-solid, multimolecular adsorption layer that is not displaced from between the solids by high pressures. Such a layer, deposited from the saturated vapor of the liquid when its pressure is appreciable, is just as effective as a gross excess of the liquid in reducing the adhesion. The stability and solidity are due to the oriented structure of the film, the polar group being fixed to the solid surface. The perfection of orientation is greatest next to the solid surface. With compounds having a polar group on one end of a hydrocarbon chain, an appreciable period of time is necessary for the oriented condition to establish itself; there is no such latent period and therefore no orientation with paraffin hydro-

<sup>9</sup> *J. Phys. Chem.*, **37**, 543 (1933).

<sup>10</sup> Hardy, *et al.*, *Phil. Mag.*, **38**, 32, 49 (1919); **40**, 201 (1920); *Proc. Roy. Soc.*, **A100**, 550, 573; **101**, 487, 492 (1922); **104**, 25 (1923); **108**, 1 (1925). Cf. also, studies of adhesion, *ibid.*, **112**, 62 (1926); **118**, 209 (1928).

carbons. During the latent period, the adhesion and static-friction coefficient fall. Over a considerable range (ca. 100°) temperature has no appreciable effect upon the adsorbed film, at least as far as static friction is concerned; there is further no discontinuity in the lubricating properties of the film at the melting temperature of the lubricant in bulk. Below the melting point, however, the latent period of orientation is very long unless reduced by mechanical working. The lubricating efficiency of the adsorption layer increases with decreasing thickness of film until the lubricating film is apparently but two molecules thick, i.e., until the adsorption layer on each solid surface is unimolecular. Among the homologous series of normal paraffin derivatives, the effect of chemical composition in determining the reduction of adhesion is surprisingly simple. Each solid surface is characterized by a friction value, depending upon its chemical character and physical state. The polar group of the lubricant reduces the adhesion by an absolute amount that depends on the character of the group but not of the solid. Each CH<sub>2</sub>-group in the hydrocarbon chain has an additional shielding effect that depends only on the polar group of the molecule, not on the solid or the position of the C-atom in the chain.<sup>11</sup> In brief, the frictional coefficient  $\mu$  is given by  $\mu = b_1 + b_2 - d - cN$ , where  $b_1$  and  $b_2$  are constants specific to the materials of the two solid surfaces,  $d$  and  $c$  are constants determined by the chemical type of the lubricant, and  $N$  is the number of CH<sub>2</sub>-groups in the lubricant.

(51) **Adsorption in Ionic Systems:** Adsorption from even the simplest of electrolyte solutions is more complex than from nonelectrolyte solutions because of the increase in the number of constituents in the solution and the electrical interaction between the surface and the ions. It is useful to distinguish between the adsorption of electrolytes by nonpolar solids, like carbon, which possess atomic or molecular lattices, and by ionogenic solids, as the inorganic salts, which consist of interpenetrating ionic lattices held together by electrostatic forces. It has been found that adsorption on charcoal is extremely dependent upon the presence of ash-forming constituents and adsorbed gas.<sup>1</sup> It now appears that ash-free, gas-free active carbon adsorbs neither strong acids nor strong bases in quantities that are detectable by ordinary analytical methods. After coming in contact with oxygen, such carbon behaves like an oxygen electrode, adsorbing strong acids positively and strong inorganic bases negatively. In the presence of hydrogen and with oxygen rigorously excluded, the same kind of carbon functions as an hydrogen electrode, adsorbing strong bases but not acids. In highly dissociated, inorganic salt solutions the gas-laden carbons bring about hydrolysis, the acid being adsorbed and the base liberated in oxygen, and the opposite occurring in hydrogen.

<sup>11</sup> Cf. a similar condition for the reduction of the surface tension of water by homologous compounds, p. 575.

<sup>1</sup> Odén, *et al.*, *J. Phys. Chem.*, **25**, 311, 385 (1921); Miller, *Fifth Colloid Symposium* (1927), p. 55; Frumkin, *et al.*, *Ber.*, **60**, 1816 (1927); *Z. physik. Chem.*, **141A**, 141, 158, 219 (1929).

(52) **The Adsorption of Electrolytes by Ionogenic Solids:**<sup>1</sup> The analytical chemist has long been familiar with the retention of foreign electrolytes by inorganic precipitates.<sup>2</sup> A number of rules have been formulated to correlate experimental observations, but because of the complexity of the phenomena, exceptions are not difficult to find. Adsorption and coprecipitation methods are especially important in the study of radioactive isotopes which either have very short lives or are so difficult to obtain that it is not possible to study their pure salts. The first systematic study of the behavior, in precipitation reactions, of minimal amounts of radioactive atomic types was made by Fajans and his coworkers.<sup>3</sup> The "precipitation rule" formulated in 1913 by Fajans states: "The lower the solubility of the compound formed by the radioelement as cation, with the anion of the precipitate, the greater is the amount of the radioelement carried down." For example, bismuth isotopes are carried down with barium carbonate and with lead hydroxide because bismuth carbonate and bismuth hydroxide are very slightly soluble. On the other hand, bismuth isotopes are not carried down with barium sulfate or lead sulfate in acid solutions because bismuth sulfate dissolves readily in acid solutions. Paneth<sup>4</sup> observed that adsorption on pre-formed precipitates followed the same rule and so the extended rule is often called the Fajans-Paneth precipitation and adsorption rule. That this rule is only a qualitative one is illustrated by the data of Table XIX<sup>5</sup> on the adsorbability and insolubility of a series of silver salts.

The exceptions to this rule as, for example, the fact that the lead isotope thorium-B is not brought down with a precipitate of mercuric iodide although lead iodide is very slightly soluble, led Hahn,<sup>6</sup> in 1926, to the conclusion that low solubility alone could not be the sole condition determining the carrying down of these extremely small amounts of material. Hahn suggested that the tracer component would be carried down with the precipitate independent of the conditions of precipitation—such as speed and excess of precipitant—only if the tracer component were incorporated isomorphously, or at least uniformly, in the precipitate. This can be used to explain the exception to the Fajans-Paneth rule given above. In addition to true coprecipitation, tracer amounts may be carried down by adsorption and the main characteristic of the latter is that the quantity carried down depends markedly upon the conditions of precipitation. Hahn's adsorption law may be stated as follows: "An ion, at any desired dilution, will be adsorbed by a precipitate if that precipitate has

<sup>1</sup> Detailed summaries of investigations in this field have been given by Weiser in his three volume *Inorganic Colloid Chemistry* (New York: John Wiley and Sons, Inc.), Vol. 1, *The Colloidal Elements* (1933); Vol. 2, *The Hydrous Oxides and Hydroxides* (1935); Vol. 3, *The Colloidal Salts* (1938).

<sup>2</sup> Cf. *Die Adsorption*, collection of van Bemmelen's scientific papers edited by Ostwald (Dresden: Steinkopf, 1910).

<sup>3</sup> Fajans, *Radioelements and Isotopes* (New York: McGraw-Hill Book Co., Inc., 1931).

<sup>4</sup> This work was reviewed in Paneth, *Radioelements as Indicators* (Ithaca, N. Y.: Cornell University Press, 1928).

<sup>5</sup> Beekley and Taylor, *J. Phys. Chem.*, 29, 942 (1929).

<sup>6</sup> Hahn, *Applied Radiochemistry* (Ithaca, N. Y.: Cornell University Press, 1936).

TABLE XIX

ADSORPTION OF SILVER SALTS BY SILVER IODIDE AND THE SOLUBILITY RULE

	Millimoles adsorbed/g AgI at 25°C and equil. concn. of 0.005 M	Relative solubilities
Benzoate.....	0.0074	1.4
Acetate.....	0.0065	8.2
Nitrite.....	0.0057	3.2
Bromate.....	0.0042	1.0
Naphthalene sulfonate.....	0.0037	4.8
Benzene sulfonate.....	0.0029	170
Nitrate.....	0.0026	1860
Chlorate.....	0.0021	100
Ethyl sulfate.....	0.0018	1540
Perchlorate.....	0.0013	3240

acquired a surface charge opposite in sign to the charge on the ion to be adsorbed, and if the adsorbed compound is slightly soluble in the solvent involved." The initial basis of this law was the experiments of Lottermoser<sup>7</sup> with solutions of silver halides, and the practical application of his results by Fajans and von Beckerath.<sup>8</sup> If calcium sulfate (gypsum) is precipitated in an excess of sulfuric acid, the sulfate ions are adsorbed and the microscopic gypsum crystals become negatively charged. If an excess of calcium chloride is used, the calcium ions are adsorbed and the crystals become positively charged. According to Hahn's adsorption rule, a cation forming a slightly soluble sulfate is precipitated most completely if the precipitate is formed with an excess of sulfuric acid. Table XX<sup>9</sup> shows that this is confirmed with experiments with thorium-B.

The effect of charge on the adsorption process is also illustrated by the "adsorption indicators" described by Fajans<sup>10</sup> and his students. In this

TABLE XX

ADSORPTION AS INFLUENCED BY THE CHARGE ON THE PRECIPITATE. RAPID  
PRECIPITATION OF GYPSUM IN PRESENCE OF ALCOHOL AND  
OF THORIUM-B (LEAD)

<i>Precipitant</i>	<i>ThB adsorbed, in per cent</i>
5 per cent excess of H <sub>2</sub> SO <sub>4</sub> .....	88.0
10 per cent excess of H <sub>2</sub> SO <sub>4</sub> .....	92.2
10-fold excess of H <sub>2</sub> SO <sub>4</sub> .....	98.4
10 per cent excess of CaCl <sub>2</sub> .....	5.2
7-fold excess of CaCl <sub>2</sub> .....	1.7

<sup>7</sup> *J. prakt. Chem.*, **72**, 39 (1905); *ibid.*, **73**, 374 (1906).

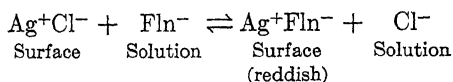
<sup>8</sup> *Z. physik. Chem.*, **97**, 478 (1921).

<sup>9</sup> Hahn, *op. cit.*, p. 93.

<sup>10</sup> Fajans and Hassel, *Z. Electrochem.*, **29**, 495 (1923); Fajans, *Radioelements and Isotopes* (1931).



method a dye, such as the sodium salt of fluorescein is added to a silver nitrate solution which is to be titrated with a sodium chloride solution. The silver chloride formed before the equivalence point is reached adsorbs silver ions which are present in excess in the solution. Simultaneously an equivalent number of fluorescein ions is adsorbed at the surface of the silver chloride particles, whereby the dye ions are deformed, the process being accompanied by an intense change of the color to red. When the equivalence point is reached, all the adsorbed silver is removed from the surface and the adsorbed fluorescein ions return to the solution which regains its yellowish red color and fluorescence. The behavior of adsorption indicators may be explained on the basis of an exchange adsorption between lattice ions and dye ions of the same sign at the surface of the particles.<sup>11</sup> If silver chloride which does not contain either an excess of adsorbed silver or of adsorbed chloride is shaken with a solution of the sodium salt of fluorescein ( $\text{Fln}^-$ ), a slight adsorption of the ions takes place, and an equivalent amount of chloride ions are sent into solution, viz.,



In this particular case there is only a slight replacement of chloride ions by fluorescein ions, but if a slight excess of silver ions is added, the chloride concentration decreases sharply favoring a replacement of the chloride ions in the surface by dye ions, resulting in a reddish coloration of the precipitate. A number of factors affect the equilibrium, and Hahn has concluded that when the adsorption compounds are very slightly soluble and when the ions involved have strong polarization, the foreign ions can be adsorbed even when the resulting precipitate has a charge of the same sign, so that the adsorption law does not hold in these cases.

(53) **Radioactive Methods for Determining the Surface Area of Inorganic Precipitates:** Paneth<sup>1</sup> used ThB (lead isotope) to determine the surface of lead sulfate precipitates by allowing the isotope to distribute itself proportionally among the lead atoms on the surface of the adsorbent and in the solution. At equilibrium, which is reached rather quickly when the precipitate is kept suspended in water until it is used, the ratio of the ThB atoms on the surface and in the solution may be determined by measurements of the diminution in the radioactivity of the solution as compared with that of the control solution; this ratio is equal to the ratio of the lead ions on the surface and in solution, i.e.,

$$\frac{\text{ThB (on surface)}}{\text{ThB (in solution)}} = \frac{\text{Pb (on surface)}}{\text{Pb (in solution)}} \quad (53.1)$$

<sup>11</sup> Kolthoff, *Chem. Rev.*, **16**, 87 (1935).

<sup>1</sup> Paneth, *Radio Elements as Indicators* (1928); *Z. Electrochem.*, **28**, 113 (1922); Paneth and Vorwerk, *Z. physik. Chem.*, **101**, 445 (1922).

Since the concentration of the lead ions in solution may be determined analytically, the number of molecules on the surface may be computed from Equation (53.1), and Paneth has found practically the same value for the specific surface independent of the ThB and lead ion concentrations. The method has been extended to the determination of the surface area of precipitates for which no radioisotope of the element is available, by using a radioisotope with which the cation in the precipitate is isomorphic. Marc<sup>2</sup> showed that a given amount of lead sulfate can adsorb only a certain maximum amount of the red dyestuff *ponceau*, and on the basis of area determinations with ThB, Paneth concluded that the dyes reach maximum adsorption before the whole of the surface is covered with a monomolecular layer.

(54) **Recent Applications of Adsorption to Radiochemistry:** In radiochemistry a substance added to remove a radioisotope from solution is spoken of as a carrier, and much has been learned about the more difficultly prepared isotopes using carriers for all the precipitations. For example, neptunium ( $_{93}\text{Np}^{239}$ ) may be carried on  $\text{LaF}_3$  in the  $\text{Np}^{\text{III}}$  form but is not carried after it has been oxidized to  $\text{Np}^{\text{IV}}$ .<sup>1</sup> One of the most important applications of the carrier technique to chemical separation was the separation of small amounts of plutonium ( $_{94}\text{Pu}^{239}$ ) from large amounts of radioactive fission products and unchanged uranium from the pile chain reaction.<sup>2</sup> Such processes involve a precipitation of Pu with a certain compound as carrier, then dissolution of the precipitate, oxidation of the plutonium to the  $\text{Pu}^{\text{VI}}$  state, and reprecipitation of the carrier compound with impurities while the  $\text{Pu}^{\text{VI}}$  remains in solution. Successive oxidation-reduction cycles are carried out until the desired decontamination is achieved.

(55) **Exchange Adsorbents:**<sup>1</sup> The first observations on base-exchange phenomena are generally accredited to Way,<sup>2</sup> who studied the adsorption of cations by soils, and to Eichorn,<sup>3</sup> who discovered that the bases were mutually exchangeable. Subsequent research devoted to the cation exchange properties of zeolites and humus materials led to the commercial application of zeolites and acid-treated peat, lignite or brown coal to water softening and the development of synthetic gel zeolites. In the case of the acid-treated humic substances, sulfonated coal, for example, the material is regenerated with dilute acid, and the exchange is a replacement by hydrogen for the cations in the water being treated, or the material may be regenerated with sodium ions, so that the exchange is a replacement of sodium ions for the cations ions present in the water. For the exchange of anions, dolomite, heavy metal silicates, horn, wool, and alkali-treated asphalt have been used.

<sup>2</sup> *Z. physik. Chem.*, **75**, 910 (1911).

<sup>1</sup> McMillan and Abelson, *Phys. Rev.*, **57**, 1185 (1940).

<sup>3</sup> Smyth, *Atomic Energy for Military Purposes* (Princeton: Princeton University Press, 1945).

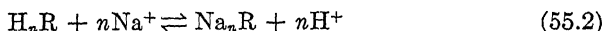
<sup>1</sup> For reviews on this subject, see Myers, in Kraemer, *Advances in Colloid Science* (1942), Vol. I, p. 317; Myers, Eastes, and Myers, *Ind. Eng. Chem.*, **31**, 1138 (1939).

<sup>2</sup> *J. Roy. Agr. Soc. Engl.*, **11**, 313 (1850); **13**, 123 (1852).

<sup>3</sup> *Landw. Jahrb.*, **4**, 1 (1875); *Ann. Physik*, **105**, 126 (1858).

An important advance in the field of exchange adsorbents was made by Adams and Holmes<sup>4</sup> in 1935 when they discovered that phenol-formaldehyde resins exhibited ion exchange properties. The advantage of synthetic resins for exchange adsorption, in addition to their favorable physical properties, is that the exchange properties may be varied at will by the selection of the reactants for the polymerization reaction. The condensation of polyhydric phenols, as, for example, the naturally occurring tannins, with formaldehyde yields resins which exchange calcium ions for hydrogen or sodium ions, and the exchange may be considered to take place on the phenolic hydroxyl groups. At low pH, larger capacity is obtained by the incorporation of strongly acidic groups such as alkyl or aryl sulfonic acids into the resin "lattice." Synthetic resins which exhibit anion-exchange or acid-adsorbent properties are prepared by condensing aromatic amines with formaldehyde. Quarternary ammonium and guanidino groups may be incorporated by several methods to increase the adsorptive capacity.

The exchange reactions for a cation-exchange resin may be written as



for the "sodium cycle" and the "hydrogen cycle," respectively, where  $\text{Na}_n\text{R}$  represents the cation exchange resin and  $\text{H}_n\text{R}$  its hydrogen form. The exchange reaction for an anion-exchange resin may be represented by



where X is the anion-exchange (acid-adsorbent) resin. The reaction is written in this way because there appears to be an adsorption of the acid as whole molecules.<sup>5</sup> The equilibrium expression in Equation (55.2), for example, is

$$K = \left( \frac{a_{\text{H}^+}}{a_{\text{Na}^+}} \right)^n \left( \frac{\text{Na}_n\text{R}}{\text{H}_n\text{R}} \right) \quad (55.4)$$

assuming that the activities of the adsorbed cations are equal to their mole fractions in the resinous exchanger while the activities of the dissolved cations are functions of their concentration in solution. According to this expression,  $\log(a_{\text{H}^+}/a_{\text{Na}^+})$  is linear in  $\log(\text{Na}_n\text{R}/\text{H}_n\text{R})$ . Such a graph for this exchange reaction shows that the law of mass action is followed and that the valence of the resin is unity.<sup>6</sup>

The reaction between the hydrogen derivative of the phenol-sulfonic acid type resin and calcium chloride or sodium chloride has been shown to be stoichiometric in character and the titration with alkali of the effluent from such an exchange column yields directly the concentration of the salt solution fed to the column. Ion-exchange resins have been profitably applied to the

<sup>4</sup> *J. Soc. Chem. Ind.*, 54, 1-6T (1935).

<sup>5</sup> Edwards, Schwartz, and Boudreaux, *Ind. Eng. Chem.*, 32, 1462 (1940).

<sup>6</sup> Boyd, Schubert, and Adamson, *J. Am. Chem. Soc.*, 69, 2818 (1947).

production of demineralized water,<sup>7</sup> concentration of dilute solutions of electrolytes,<sup>8</sup> and preparation of organic compounds.<sup>9</sup> An application of major importance has been in the separation of fission-produced radioisotopes and rare earths by workers on the Manhattan Project.<sup>10</sup>

(56) **Chromatography:**<sup>1</sup> The chromatographic adsorption method of analysis was originated by the Russian botanist Tswett<sup>2</sup> in 1906, but the method was latent until about 1931. Tswett discovered that if a solution of chlorophyll from leaves is poured on the top of a column of a suitable adsorbent the components of the solution are adsorbed at the top of the column and when a solvent is poured through the column, the colored band is resolved into a series of such bands which move down the column with different rates. Each band represents a component of the original mixture, and by removing the column of adsorbent and cutting it into sections, pure samples of each component may be obtained. Adsorption methods have been widely applied in organic and biological chemistry because of the strikingly high specificity of adsorption. In the case of colorless substances, observations may be made by using ultraviolet light, or by testing with different specific reagents, either on the column directly or after it has been cut into sections and extracted. Methods of more general applicability depend upon the determination of the total concentration of the solution just as it passes from the adsorption column, by measurement of the refractive index, refractive index gradient, light adsorption, conductivity or some other suitable physical property of the solution.<sup>3</sup> Such methods may be applied to adsorption from gases as well as solutions, and the usual method of representing experimental data is to plot the concentration of the solution leaving the adsorbent against the volume which has been passed through the adsorbent.

In general there are three methods of making adsorption analyses.

*Frontal Analysis:* In this method the adsorbent is first washed with pure solvent and then the solution to be analyzed is allowed to pass through. In the beginning pure solvent comes through the cell, but as soon as the adsorbent has become saturated with the least strongly adsorbed solute, this solute appears in the effluent. Figure 31a is a plot of the concentration of the effluent

<sup>7</sup> Myers and Eastes, *Ind. Eng. Chem.*, **33**, 1203 (1941).

<sup>8</sup> Beaton and Furnes, *ibid.*, **33**, 1500 (1941).

<sup>9</sup> McCready and Hassid, *J. Am. Chem. Soc.*, **66**, 560 (1944).

<sup>10</sup> Series of papers on *Ion Exchange Resins*, *J. Am. Chem. Soc.*, **69**, No. 11 (1947).

<sup>1</sup> General references: Zechmeister and Cholnoky, *Die Chromatographische Adsorption-methode* (Vienna: Verlag Julius Springer, 1938); *Principles and Practice of Chromatography* (London: Chapman and Hall, 1941); Strain, *Chromatographic Adsorption Analysis* (New York: Interscience Publishers, 1942); Tiselius, in Kraemer, *Advances in Colloid Science* (1942), Vol. 1; Clarke, in Alexander, *Colloid Chemistry* (1944), Vol. V, p. 457; Williams, *An Introduction to Chromatography* (Glasgow: Blackie & Son, Ltd., 1947); Cassidy, *et al.*, *Ann. N. Y. Acad. Sci.* XLIX, 141-326 (1948).

<sup>2</sup> *Ber. deut. botan. Ges.*, **24**, 234, 316, 384 (1906); *Ber.*, **41**, 1352 (1908); **43**, 3199 (1910); **44**, 1124 (1911).

<sup>3</sup> Tiselius, *Arkiv. Kemi. Mineral. Geol.*, **14B**, No. 22 (1940); **15B**, No. 6 (1941); Claesson, *ibid.*, **23A**, No. 1 (1946).

from a solution containing two solutes, 1 and 2, against volume passed through the column. The solution between volumes  $V_1$  and  $V_2$  contains only solute 1, and after the second step the solution passes unchanged through the filter. The heights of the steps, however, will not be a direct measure of the concentration

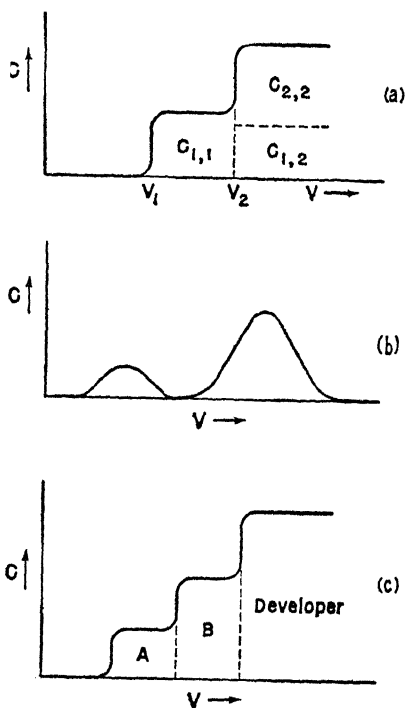


FIG. 31. Three Methods for Making Adsorption Analyses. (a) Frontal analysis. (b) Elution analysis. (c) Displacement development.

measuring  $v^0$  at a series of concentrations. In this way it is possible to fix the concentration of the solute at equilibrium beforehand, which is not possible when shaking a solution with adsorbent. Three possible types of adsorption isotherms are illustrated in Fig. 32. Using these graphs and Equation (56.1) it is possible to plot the variation of the specific retardation volume ( $v^0$ ) with concentration. In all these cases this volume assumes a constant value in dilute solutions, which may be useful for identification. Tiselius<sup>5</sup> has compiled a number of specific retardation volumes. The most common type of adsorption isotherm is I, and the decrease in retardation volume with increasing

of the original solution because solute 2, which comes second, partially displaces solute 1 from the adsorbent. However, it has been shown that the quantitative composition of a solution may be calculated if the equations of the adsorption isotherms are known.<sup>4</sup>

Some of the characteristics of frontal analysis may be derived from a consideration of the adsorption analysis of a solution containing one component of concentration  $c^0$ . The volume which passes through the adsorbent before the step appears (corrected for the volume of solution necessary to replace the solvent between the adsorbent particles at the beginning of the experiment) is called the "retardation volume" and the retardation volume divided by the weight of adsorbent is the specific retardation volume,  $v^0$ . The amount  $a^0$  of solute adsorbed on the 1 g of adsorbent has been taken from the volume  $v^0$ , so that

$$a^0 = v^0 c^0 \quad (56.1)$$

Since  $a^0$  is the amount adsorbed per gram of adsorbent in equilibrium with the solution of concentration  $c^0$ , the adsorption isotherm may be determined by

<sup>4</sup> Claesson, *loc. cit.*

<sup>5</sup> Tiselius, in Kraemer, *Advances in Colloid Science* (1942), Vol. 1.

concentration in this case may be used to explain why the front of the band moving through the adsorbent is sharp. Molecules diffusing ahead of the main front move into a region of lower concentration where the retardation volume is larger, and hence the front of low concentration moves more slowly and will be overtaken by the main front.

**Elution Analysis:** In this method a small amount of the solution to be analyzed is poured on the column and washed through with a larger volume of solvent. This causes the components to move as separate zones through the column and to appear as peaks in the plot of concentration vs. volume (Fig.

31b). The area under each peak is  $\int_{V_1}^{V_2} c dV$ , i.e., the amount of dissolved

substance, so that a quantitative analysis of the mixture is obtained by simple measurement of areas. This method is well adapted to quantitative or preparative purposes because each component may be collected in a pure state. The disadvantage of this method is that there are often long tails on the peaks, as illustrated in Fig. 32, which makes their complete separation difficult. In the case of the type I isotherm, molecules diffusing into the less concentrated region behind the band will move more slowly because of the increased retardation volume for dilute solutions and will therefore tend to form a diffuse tail. In case the isotherm is linear (II), both ends of the band will be spread by diffusion, and, in case III, the leading front will be blurred while the rear front remains sharp.

**Displacement Development:** In this method, which was introduced by Tiselius,<sup>6</sup> a solution of a substance, the "developer," which is more strongly adsorbed than any of the components of the mixture, is used to wash the column after the sample for analysis has been poured on. The mixture to be analyzed is thus forced to move in front of the developer and is separated into different zones, each of which contains one component, as illustrated in Fig. 31c. The theoretical interpretation shows that qualitative and quantitative analysis is reduced to measurements of the heights of the steps, which are characteristic of the adsorbed substances, and the lengths of the steps, which are directly

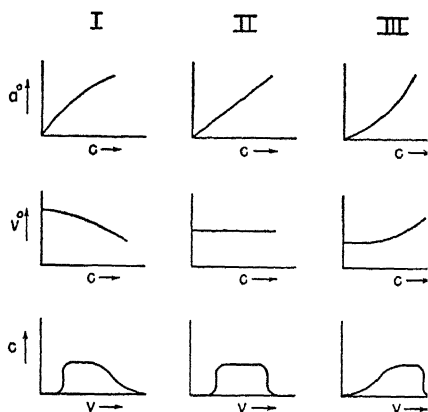


FIG. 32. The Variation in Retardation Volume,  $v^0$ , as a Function of Concentration depends upon the type of Adsorption Isotherm. The lower three diagrams indicate the results which would be obtained in elution analysis.

<sup>6</sup> Tiselius, *Arkiv Kemi Mineral. Geol.*, 16A, 18 (1943).

proportional to the amount of substance. If a substance is so strongly adsorbed that it cannot be displaced, frontal analysis is the only method available.

The theory of chromatography <sup>7</sup> has been developed to the extent that most of the phenomena observed may be explained. However, the selection of adsorbents, solvents, and displacing agents is still empirical.

Chromatographic columns may be packed with wet silica gel or starch and an immiscible organic solvent flowed through the column.<sup>8</sup> In this case the separation of the solutes depends upon their differences in partition coefficient between chloroform and water, and such chromatograms are referred to as "partition chromatograms." Such a separation process is analogous to a counter-current extraction, and Martin and Synge developed a theory expressing the efficiency of the chromatogram in terms of the number of theoretical plates of an extraction apparatus to which it is equivalent. They found that under the limited conditions in which the distribution coefficient did not change with the change in concentration of the solute, the width of the band, as predicted by their theory, was very similar to that observed experimentally. From their theory it may be shown that the partition coefficient,  $\alpha$ , of a solute is related to the rate of movement of its band in the column,  $R$ , by the following equation,

$$\alpha = \frac{A}{RA_S} - \frac{A_L}{A_S} \quad (56.2)$$

$R = \frac{\text{movement of position of maximum concentration of solute}}{\text{simultaneous movement of surface of developing phase in empty part of tube above chromatogram column}}$

$$\alpha = \frac{\text{g solute/l of non-mobile phase}}{\text{g solute/l of mobile phase}}$$

and  $A$ ,  $A_S$ , and  $A_L$  are the areas of cross section of the column, the non-mobile phase, and the mobile phase, respectively.

Mayer and Tompkins <sup>9</sup> have applied similar calculations to ion exchange columns and, since the results may be expressed very simply in their notation, their development is followed. The column is considered as being made up of a number of theoretical plates,  $p$ , each plate having an equivalent mass of resin,  $m$ , and volume of solution,  $v$ . As flow is started through the column, these  $v$ 's of solution progress down the column from plate to plate. Other symbols which will be used are:

<sup>7</sup> Martin and Synge, *Biochem. J.*, **35**, 1358 (1941); Le Rosen, *J. Am. Chem. Soc.*, **64**, 1905 (1942); **67**, 1683 (1945); **69**, 87 (1947); Wilson, *ibid.*, **62**, 1583 (1940); DeVault, *ibid.*, **65**, 532 (1943); Tiselius, *Arkiv Kemi Mineral. Geol.*, **14B**, No. 22 (1940); **15B**, No. 6 (1941); Claesson, *ibid.*, **23A**, No. 1 (1946).

<sup>8</sup> Martin and Synge, *Biochem. J.*, **35**, 1358 (1941).

<sup>9</sup> *J. Am. Chem. Soc.*, **69**, 2866 (1947).

$V = (pv)$  = volume of solution in the column.

$n$  = number of  $v$ 's that have entered into a plate up to any given time.

$F = (n/p)$  = number of  $V$ 's that have passed through the column.

$L$  = the fraction of a solute in any  $v$  of solution.

$S$  = the fraction of a solute in the solid phase of the column in any plate.

$L_{n,p}$  = the fraction of solute in solution which is in contact with plate  $p$  when the  $n$ th  $v$  has equilibrated in that plate.

$S_{n,p}$  = the fraction of solute in the solid phase in plate  $p$  when the  $n$ th  $v$  has equilibrated in the plate.

The distribution of solute in any plate may be expressed as

$$S_{n,p}/L_{n,p} = C \quad (56.3)$$

where  $C$  represents the distribution of the solute between the solution and the resin in a plate,  $p$ . To maintain material balance

$$L_{n,p} + S_{n,p} = L_{n,p-1} + S_{n-1,p} \quad (56.4)$$

The top part of the column is designated as plate zero and contains unit quantity of material being adsorbed. When the first increment of volume  $v$  enters the column it will come in contact with the fraction of solute in the zero plate which in solution ( $L_{1,0}$ ) and the fraction in the solid phase ( $S_{1,0}$ ) at equilibrium may be calculated as follows from Equations (56.3) and (56.4).

$$S_{1,0}/L_{1,0} = C$$

$$L_{1,0} + S_{1,0} = 0 + 1$$

$$S_{1,0} = \frac{C}{1+C} \quad L_{1,0} = \frac{1}{1+C}$$

The fractions  $S$  and  $L$  after  $n$  volumes  $v$  have entered the plate are

$$S_{n,0} = \frac{C^n}{(1+C)^n} \quad L_{n,0} = \frac{C^{n-1}}{(1+C)^n}$$

For the first theoretical plate

$$L_{1,1} + S_{1,1} = L_{1,0} + S_{0,1} \quad (1+C) + 0$$

$$S_{1,1}/L_{1,1}$$

$$L_{1,1} = \frac{C}{(1+C)^2} \quad S_{1,1} = \frac{1}{(1+C)^2}$$

After  $n$  volumes have entered the first plate

$$\bar{L}_{n,1} = \frac{nC^{n-1}}{(1+C)^{n+1}} \quad S_{n,1} = \frac{nC^n}{(1+C)^{n+1}}$$



Further, it can be shown that for any plate  $p$  after  $n$  volumes have entered that plate

$$L_{n,p} = \frac{(n+p-1)!C^{n-1}}{(n-1)!p!(1+C)^{n+p}} \quad (56.5)$$

$$S_{n,p} = \frac{(n+p-1)!C^n}{(n-1)!p!(1+C)^{n+p}} \quad (56.6)$$

For large values of  $n$  and  $p$  Stirling's approximation may be used.

$$L_{n,p} = \frac{1}{\sqrt{2\pi}} \frac{(p+n-1)^{p+n-\frac{1}{2}} C^{n-1}}{(n-1)^{n-\frac{1}{2}} p^{p+\frac{1}{2}} (1+C)^{p+n}} \quad (56.7)$$

It can be shown that when  $n = pC$ ,  $L_{n,p}$  in equation (56.7) will have its maximum value.

$$L_{\max} = [2\pi pC(1+C)]^{-1/2} \quad (56.8)$$

It may also be shown that the number of  $v$ 's which pass through the column before the maximum in the solute concentration has been eluted is numerically equal to the distribution coefficient  $C$ . The elution curve for a mixture which is a plot of the concentration in the eluent of the elements being separated against the volume of eluting solvent that has passed through the column can therefore be used to obtain the corresponding  $C$ 's of the materials being separated. From the maximum concentrations of the various solutes found in the eluate the number of theoretical plates in the column may be calculated using Equation (56.8). The relationship between  $C$  and the usual distribution coefficient,  $K_d$ , may be shown simply.

$$K_d = \frac{S_{n,p}/m}{L_{n,p}/v} = Cv/m \quad (56.9)$$

Since  $v/m$  is the ratio of volume of solution in the column to the mass of resin in the column,  $K_d$  may be calculated simply from  $C$ . The  $K_d$  values obtained in this way from column experiments in which low flow rates were used so as to approximate closely equilibrium conditions have been shown to be in good agreement with the values obtained in batch ion exchange experiments. In column separation processes there will always be some overlapping between the elution curves because the column must be infinitely long or the  $C$ 's must differ by infinity to secure complete separation. Using the theory outlined above it is possible to calculate the amount of any component in a mixture which may be eluted with a given per cent impurity provided the corresponding  $C$ 's and the number of theoretical plates in the columns are known.

The very high selectivity of adsorption as made use of in chromatography makes possible a number of important applications.

(1) Homogeneity tests. A substance which gives only one band with several different adsorbents and solvents is a single entity.

(2) Establishment of the identity or non-identity of two substances. A mixed chromatogram may be studied like a mixed melting point.

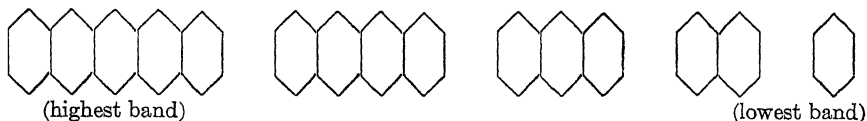
(3) Concentration of natural products or minerals occurring only at great dilutions. Such a process involves the use of a suitable adsorbent from which the desired material later may be eluted.

(4) Separation, identification, and analysis of the constituents of mixtures which are otherwise difficult to separate. A most important problem now receiving considerable attention is the analysis of protein hydrolysates.

(5) Purification of materials.

(6) Identification and control of commercial products on a routine basis.

(7) Determination of molecular structure. Generally speaking, adsorbability of organic compounds increases with the number of polar groups. In the polyene series  $C_6H_5-(CH=CH)_n-C_6H_5$  the larger  $n$ , the stronger the adsorption. In the polycyclic hydrocarbon series the order of the bands is as shown below.



The data in Table XXI, obtained by Claesson,<sup>10</sup> indicate the accuracy obtainable by chromatographic analysis. Much smaller amounts may be used

TABLE XXI  
RESULTS OF CHROMATOGRAPHIC ANALYSES

Frontal analyses of mixtures of fatty acids in ethanol adsorbed on active carbon			Displacement development of mixtures of hydrocarbons in gas phase on active carbon using ethyl acetate "developer"		
Acid	Known	Found	Hydrocarbon	Known	Found
Octanoic	20%	21%	<i>n</i> -Hexane	20.4%	19.7%
Decanoic	20	19	<i>n</i> -Heptane	79.6	80.3
Tetradecanoic	20	20			
Hexadecanoic	40	41	<i>n</i> -Pentane	5.6	5.7
			<i>n</i> -Hexane	33.0	32.8
			<i>n</i> -Heptane	61.4	61.5
			Cyclohexane	46.6	46.6
			Benzene	53.6	53.4

than in fractional distillation; for analysis of the gaseous mixtures Claesson used only about 200 mg.

Filter paper has proved to be a useful support for the stationary phase in partition chromatography. If the order or velocity of bands is different when

<sup>10</sup> *Thesis*, Upsala, 1946.

different solvents are used a two-dimensional chromatogram may be prepared by using the first solvent to spread the substances along a line close to and parallel to one edge of the paper. The sheet is then dried and a second solvent is used to develop the chromatogram perpendicular to the original direction.<sup>11</sup>

#### ELECTROKINETIC PHENOMENA<sup>12</sup>

Although the properties of the electric double-layer are more susceptible to rational treatment under static equilibrium conditions, manifestations of the double-layer under dynamic conditions have received more attention in the development of colloid science.

In 1808, Reuss<sup>13</sup> reported that an electrical field across a wet clay diaphragm caused water to flow through the diaphragm toward the cathode and suspended clay particles to move, at the same time, toward the anode. During the following years, a number of qualitative or semiquantitative experiments of an analogous sort were made, but Wiedemann<sup>14</sup> carried out the first systematic experiments and established the empirical laws describing the phenomena as they occur not only in compressed powder partitions, but also in single glass capillaries. In the course of further investigations, Quincke<sup>15</sup> observed that an electrical potential is produced when water is forced through a diaphragm, and suggested<sup>16</sup> that an electric double-layer at the surface of the particles was responsible for these different effects. Quincke also refined the study of the behavior of suspended particles in an electric field by following microscopically the motion of single particles. He and Wiedemann, working independently, examined a great many different liquids and solids, used as compressed fine-powder diaphragms. Later, in 1880, Dorn<sup>17</sup> discovered that potential differences also occur when particles fall through water.

Following Freundlich, these four effects, all involving electrical potentials and tangential motion at an interface between a continuous fluid phase and a second phase, are called "electrokinetic phenomena." The four effects are (a) electrophoresis, in which a motion of particles through stationary liquids is caused by an applied electric field and its converse; (b) the Dorn effect (sedimentation potential) in which an electric field is set up by the motion of particles through stationary liquids; (c) electroosmosis in which a flow of liquid along stationary walls is caused by an applied emf; and (d) its converse, the streaming potential which results from an externally impressed tangential flow

<sup>11</sup> Martin and Syngé, *Advances in Protein Chemistry* (New York: Academic Press, Inc., 1945), Vol. II.

<sup>12</sup> General references: Abramson, *Electrokinetic Phenomena and Their Application to Biology and Medicine* (New York: Chemical Catalog Co., 1934); MacInnes, *The Principles of Electrochemistry* (New York: Reinhold Publishing Corp., 1939), chap. 23; General Discussion, *Electrical Double-Layer*, *Trans. Faraday Soc.*, 36 (1940).

<sup>13</sup> *Mem. Soc. Imp. Naturalistes Moscou*, 2, 327 (1809).

<sup>14</sup> *Ann. Physik*, 87, 321 (1852).

<sup>15</sup> *Ibid.*, 107, 1 (1859).

<sup>16</sup> Quincke, *ibid.*, 113, 513 (1861).

<sup>17</sup> *Ibid.*, 10, 46 (1880).

of liquid. In general, electrophoresis and sedimentation potentials may be observed with solid, liquid or gas particles suspended in a liquid, whereas electroosmosis and streaming potentials can be observed only at a solid interface provided by a porous diaphragm or a single capillary through which the liquid can pass as it moves from one electrode compartment to the other. As a matter of fact, electrokinetic effects of a sort may occur when the continuous liquid phase is replaced by a gas (e.g., in the electrical precipitation of smokes and clouds, or the electrification of an orifice from which gas is allowed to escape), but they are not commonly considered with electrokinetic phenomena because of differences in the nature of the double-layer and in the mechanism of the charging process.

(57) **Helmholtz Theory of the Electric Double-Layer:** Building on Quincke's ideas of the double-layer, Helmholtz<sup>1</sup> worked out the first mathematical theory for electroosmosis in a single insulating capillary tube of uniform bore. He postulated that a double-layer exists in the liquid adjacent to the capillary wall, one layer, the "inner" one, adhering firmly to the capillary, the "outer" layer residing nearby in the body of the liquid and moving with it as shown in Fig. 33. In a streaming potential experiment, a flow of liquid through the capillary drags the outer layer with it and gives rise to a potential difference between the two ends of the tube. In an electroosmotic experiment, a potential difference parallel to the tube axis tends to separate the oppositely charged regions. Since the capillary wall and adhering charged layer are fixed, the outer layer moves, dragging the column of liquid with it. When the electrical forces balance the viscous forces, the whole column of liquid will move through the capillary with a uniform rate, in effect being pulled by the skin. The shear of the liquid is supposed to be localized between the two charged layers, with no slippage at the capillary wall, and the liquid in the double-layer is assumed to retain its normal hydrodynamical and electrical properties. Within the double-layer region, the external electrical field is assumed to be superposed upon that within the double-layer, which is considered equivalent to a plane parallel-plate condenser of constant capacity. The thickness of the double-layer, i.e., the distance between the plates of the equivalent condenser, is negligible relative to the radius of curvature of the interface. On these assumptions, Helmholtz obtained an equation for the velocity of the liquid which may also be obtained, admittedly in less rigorous fashion, by a simpler derivation due to Perrin.<sup>2</sup>

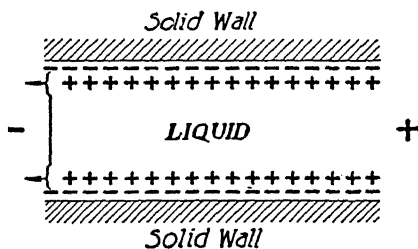


FIG. 33. Original Helmholtz Double-Layer in Capillary. Adhering layer of negative electricity at wall; positive layer of electricity in liquid causing electroosmosis to the cathode.

<sup>1</sup> *Ibid.*, 7, 337 (1879).

<sup>2</sup> *J. chim. Phys.*, 2, 607 (1904).

If the surface charge density per square centimeter on the movable layer is  $\sigma$  and the potential gradient along the tube of length  $l$  is  $X = E/l$ , the electrical force causing motion is  $\sigma X$ . The motion is resisted by the frictional resistance within the double layer, which is equal to the product of the viscosity  $\eta$  and the velocity gradient  $U/d$ , where  $U$  is the velocity of the movable layer, and  $d$  is the thickness of the double-layer. In the steady state and in the absence of turbulent flow  $\sigma X = \eta U/d$ , so that

$$u = U/X = \sigma d/\eta \quad (57.1)$$

The velocity in a field of unit strength is called the electrophoretic mobility,  $u$ , usually expressed in the units square centimeters per volt per second. The electric moment of the double-layer per unit area is  $\sigma d$ . On the other hand, the potential  $\zeta$  of the cylindrical condenser is given by the expression

$$\zeta = 4\pi\sigma d/\epsilon \quad (57.2)$$

where  $\epsilon$  is the dielectric constant in the double-layer. Eliminating  $\sigma d$  and rearranging gives

$$u = U/X = \zeta\epsilon/4\pi\eta \quad (57.3)$$

where  $\zeta$  is the so-called "zeta" or electrokinetic potential. For a given liquid,  $u$  is thus proportional to  $\zeta$  and  $\sigma d$ , and is independent of the diameter or length of the capillary or the voltage difference across it. The total volume  $v$  of liquid transported per sec. is equal to  $Uq$ , where  $q (= \pi R^2)$  is the cross-sectional area of the capillary, so that

$$v = Uq = \zeta\epsilon Xq/4\pi\eta \quad (57.4)$$

Since  $X = I/\lambda q$ , where  $I$  is the current and  $\lambda$  is the specific conductance of the liquid in the capillary,

$$v = \zeta\epsilon I/4\pi\eta\lambda \quad (57.5)$$

or, in other words, the total transport of a given liquid in contact with a certain solid is determined solely by the current. In order to avoid surface conductivity effects  $\lambda$  should be measured with the liquid in the capillary rather than in bulk.

If the electroosmotic flow is opposed by a hydrostatic pressure  $P$ , it may for simplicity be assumed that electroosmotic transport occurs along the walls of the capillary and a reverse flow, under the hydrostatic head, along the axis of the capillary. According to Poiseuille's law the rate of reverse flow  $U_p$  is

$$U_p = \frac{\pi R^4 P}{8\eta l} = \frac{P}{W} \quad (57.6)$$

where  $W$  defines the resistance to flow.

Assuming the thickness of the region where the liquid travel is in the direction of the electroosmotic flow to be negligible compared to the capillary radius,

we may set equations for  $U_p$  and  $U$  equal to each other, the  $R$ -values in both being assumed equal, and solve for  $P$ ; thus,

$$\frac{2\zeta\epsilon E}{\pi R^2} = \frac{\zeta\epsilon IW}{4\pi\eta\lambda} \quad (57.7)$$

The resistance to flow  $W$  may be determined by separate experiments correlating pressure and the rate of flow,  $U_p$ .

When a streaming potential experiment is made, the liquid which is forced through the capillary carries the movable layer with it, thus tending to separate its charge from the fixed layer on the wall. According to Newton's law (p. 559), the shearing stress =  $\eta \times$  velocity gradient. The stress on the movable layer is  $P(R - d)/2l$ , where  $P$  is the driving pressure. The velocity gradient, as stated above, is  $U_p/d$ , where  $U_p$  is the velocity of the movable layer. It follows, therefore, that  $P(R - d)/2l = \eta U_p/d$ , or

$$U_p = \frac{PRd}{2l\eta} \quad (57.8)$$

when  $d^2$  is negligible compared to  $Rd$ . The motion of the movable layer constitutes a current and produces a difference of potential across the length of capillary, which in turn causes a compensating current to flow backwards through the liquid in order to prevent the accumulation of an appreciable charge at the ends of the capillary. The current  $I_s$ , due to streaming, is given by the product of the total charge on the movable layer ( $2\pi R\sigma$ ) and its velocity  $U_p$ . Inserting the value of  $U_p$  and the relation between the electric moment and  $\zeta$  for the condenser, i.e.,  $Ud = \zeta\epsilon/4\pi$ , gives

$$I_s = \zeta\epsilon R^2 P / 4\eta l \quad (57.9)$$

The return current  $I_E$  due to the potential  $E$  produced is  $E \div$  resistance of liquid in capillary, or  $I_E = E\lambda\pi R^2/l$ . Upon equating  $I_s$  and  $I_E$  and solving for the streaming potential  $E$ , the result, using Equation (57.2), is

$$E = \frac{\zeta\epsilon P}{4\pi\eta\lambda} = \frac{\sigma d P}{\eta\lambda} \quad (57.10)$$

The equation is limited to conditions of non-turbulent flow (which has been perhaps sometimes overlooked) and, in this instance also, to avoid difficulties with surface conductivity,  $\lambda$  is the value measured in the capillary tube. Furthermore, the thickness of the double-layer must be negligible relative to the capillary radius. It is also possible that a correction should at times be made for the electroosmosis resulting from the streaming potential.<sup>3</sup>

The Helmholtz equation for electrophoresis follows directly from the above discussion of electroosmosis, since the argument really concerns the relative motion of solid and liquid at a long cylindrical interface oriented parallel to the

<sup>3</sup> Butler, *Chemical Thermodynamics* (4th ed.; London: The MacMillan Co., 1946).

electric field. The solid and liquid phases at the interface may be exchanged, giving a solid particle of the same size as the liquid in the capillary, without affecting the relative velocity of the two parts of the double-layer. The electrophoretic velocity is therefore equal to the electroosmotic velocity, and the same restrictions regarding the magnitude of the double-layer thickness relative to the radius of the curvature of the interface apply to both.

The theory of Helmholtz was refined by Smoluchowski <sup>4</sup> who pointed out that the Helmholtz equation is applicable to a particle of any shape or orientation as well as to an oriented cylinder, provided only (1) that the particle is of "easy" shape, and (2) that the radius of curvature of all points on its surface is much greater than the thickness of the double layer. He also showed that electroosmotic and streaming potential equations for a single capillary are also applicable to multiple capillaries of any size and shape and, therefore, also to porous diaphragms of compressed powders, provided the pores are much larger than the thickness of the double-layer. Similarly, the electrophoretic equation, under comparable restrictions, is applicable to particles of any size or shape.

As J. J. Thomson and Hardy pointed out, the presence of an electric double-layer on suspended particles or on a capillary wall increases the resistance to flow in the system. Smoluchowski <sup>5</sup> calculated the resulting effect on the viscosity of a suspension and found that the intrinsic viscosity (see p. 561) is increased in accordance with the equation

$$\frac{\Delta[\eta]}{[\eta]} = \frac{1}{16\lambda\eta_0} \left( \frac{\zeta e}{\pi r} \right)^2 \quad (57.11)$$

where  $\Delta[\eta]/[\eta]$  is the fractional increase of intrinsic viscosity,  $\eta_0$  is the viscosity of the pure solvent, and  $r$  is the particle radius. Here, too, the thickness of the double-layer must be much less than the radius of the particle. This so-called "electroviscous effect" should also lead to departures from Newton's law, owing to variation of the effect with rate of flow.

Since, in general, there are no independent methods of measuring the zeta potential, the electric moment, the charge density or the thickness of the double-layer, the above electrokinetic equations can not be directly tested experimentally. In effect, the equations provide definitions for these unmeasurable quantities, and through them describe the interrelationship of the different types of electrokinetic effects for a given interface. The work of Wiedemann and of Quincke had already empirically established the laws expressed in the equations regarding the interrelationship of the physical factors, such as electroosmotic velocity and pressure, streaming potential, electrophoretic velocity, potential gradient, current, dimensions of capillary, and porosity of porous diaphragm. Some efforts were made to vary also the dielectric constant, viscosity and conductivity, but, in general, these were not successful since such changes involve changing the liquid, which in turn changes

<sup>4</sup> *Bull. Acad. Sci. Cracovie*, 183 (1903); Smoluchowski, in Graetz, *Handbuch der Elektrizität und des Magnetismus* (Leipzig: Barth, 1914), Vol. 2.

<sup>5</sup> *Kolloid Z.*, 18, 190 (1916).

also  $\zeta$ ,  $\sigma$ , and  $d$  to an unknown degree. In spite of these uncertainties, most investigators concerned with the study of the effect of the nature or composition of the two phases meeting at the interface upon electrokinetic behavior have calculated  $\zeta$  or  $\sigma d$  for comparison purposes.<sup>6</sup>

(58) **Electrokinetic and Electrochemical Potentials:** The potential at the interface between two adjacent phases of different potential does not vary linearly from the high to low values as assumed by Helmholtz, but may be represented by Fig. 34a. In this figure  $\psi$  is the electrical potential, and the total potential difference between the phases is the phase potential or thermodynamic potential,  $E$ . On the surface of the solid is a thin layer of the liquid phase which is held so tightly that temperature motion in this layer may be neglected. The outer edge of this layer is called the "rigid boundary" (R.B.), and it is the potential difference between this boundary and the interior of the liquid which is called the "zeta potential,"  $\zeta$ . The theory of the diffuse double layer is a theory of the zeta potential only and does not include the phase potential,  $E$ . The electric force on a unit positive ion is equal to the negative space derivative of the potential (Fig. 34b), and the charge density is equal to the negative second derivative of the potential by Poisson's equation (59.3) (Fig. 34c). The excess of positive charges on the high-potential side of the boundary and the excess of negative charge on the low-potential side make up the "diffuse double layer." The whole subject has been outstandingly reviewed by Verwey and Overbeek.<sup>1</sup>

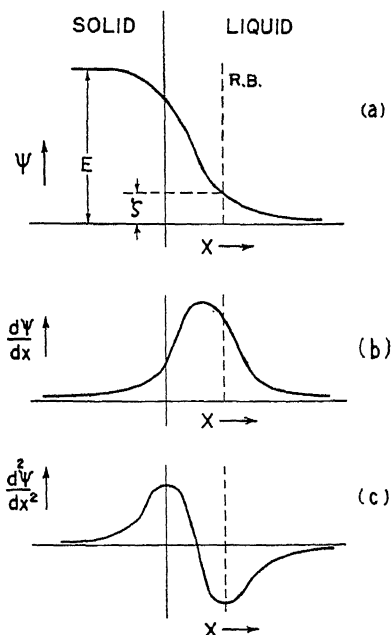


FIG. 34. Modern Concept of the Electric Double Layer. (a) Variation in potential through the double layer. (b) Variation in field strength through the double layer. (c) Variation in charge density through the double layer.

<sup>6</sup> In calculations with the above equations, it may be pointed out that all quantities should be in cgs units, the electrical quantities being in addition in electrostatic units. Then  $P$  is in dynes per square centimeter,  $\zeta$ ,  $E$  and  $X$  in volts/300;  $\lambda$  in ohms<sup>-1</sup>  $\times 9 \times 10^{11}$ ;  $I$  in amperes  $\times 3 \times 10^9$ ;  $\sigma$  in coulombs  $\times 3 \times 10^9$ , or number of electrons  $\times 4.8 \times 10^{10}$ , or faradays  $\times 2.89 \times 10^{14}$ . To illustrate the order of magnitude, Quincke found for the interface glass||distilled water,  $u = 30 \times 10^{-5}$  cm<sup>2</sup>/sec/volt, which corresponds to a zeta potential of about 40 millivolts or an electric moment of about  $1.6 \times 10^6$  electron/cm. For comparison, mobilities of common ions, at infinite dilution and room temperature average about  $50 \times 10^{-5}$  cm<sup>2</sup>/sec/volt with the exception of the much larger values for  $H^+$  and  $OH^-$ .

<sup>1</sup> *Theory of the Stability of Lyophobic Colloids* (New York: Elsevier Publishing Co., 1948).



(59) **Diffuse Double Layer:** Helmholtz's theory, involving a rigid electric double-layer, gives an interrelationship between the potential of the double layer and the electric moment per unit area, but it provides no insight regarding the manner in which charge density or thickness of the double-layer may vary. This requires a more detailed picture of the double-layer.

The first important step in the elaboration of an improved theory in this respect was taken by Gouy,<sup>1</sup> who considered that the ions of the outer layer form a diffuse ionic atmosphere under the opposing forces of electrostatic attraction toward the charged inner layer fixed to the interface and the diffusive forces due to thermal agitation. A dynamic equilibrium is imagined to exist, comparable to a sedimentation equilibrium in a gravitational field. In the gravitational field, the potential at any point is  $gh$ , where  $h$  is the height, and the gravitational force, as we have seen (p. 542), on a single particle is  $mgh$ . In the diffuse ionic layer, the electrical potential is  $\psi$ , which is as yet an undetermined function of distance from the charged interface, and the electric force on the ion is  $ze\psi$ , where  $z$  is its valence and  $e$  is the electronic charge. In accordance with the Maxwell-Boltzmann principle, the number of particles (in the gravity case), or of ions (in the diffuse ionic layer) is an exponential function of the force at every level. Explicitly, for the ionic atmosphere, the number  $n_i$  of ions of type  $i$  per cubic centimeter at any point near a positive charge is related to their valence ( $z_i$ ) and the number  $n_{0i}$  of the ions per cubic centimeter in the body of the solution (where  $\psi$  can be considered zero) by the expression

$$n_i = n_{0i}e^{-z_ie\psi/kT} \quad (59.1)$$

Here, the sign of  $\psi$  is taken as the same as that of the charge to which the potential is due;  $z$  is taken as positive for positive ions and negative for negative ions; and only the absolute magnitude of  $e$  is used. The charge density due to each type of ion in the given volume is equal to the product  $n_iz_ie$ , and the net charge density  $\rho$  is equal to the sum of the various contributions, or

$$\rho = \sum n_iz_ie = e\sum n_{0i}z_ie^{-z_ie\psi/kT} \quad (59.2)$$

Thus  $\rho$  will have a sign opposite that of the potential  $\psi$ . The net charge density is also related to the potential by Poisson's equation

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} = \nabla^2\psi = \frac{-4\pi\rho}{\epsilon} \quad (59.3)$$

Elimination of  $\rho$  between these two equations gives the general differential equation for the diffuse electric double layer, viz.,

$$\nabla^2\psi = \frac{-4\pi e}{\epsilon} \sum n_{0i}z_ie^{-z_ie\psi/kT} \quad (59.4)$$

This equation has been solved directly only for plane surfaces, which may be assumed to refer also to large radii of curvature in general. The usual restric-

<sup>1</sup> *J. phys. rad.*, 9, 457 (1910).

tions put on the equation is to limit the electrolytes to a single symmetrical valence type, e.g., uni-univalent, bi-bivalent, etc. For many cases, it is unnecessary to distinguish between a single electrolyte or a mixture, provided the electrolytes in the mixture are all of the same valence type. The symmetrical valence type will be considered first; Equation (59.4) may then be written

$$\begin{aligned}\nabla^2\psi &= \frac{4\pi en_0z}{\epsilon} (e^{-ze\psi/kT} - e^{ze\psi/kT}) \\ \frac{8\pi en_0z}{\epsilon} \sinh \frac{ze\psi}{kT} & \\ \frac{8\pi e^2 n_0 z^2 \psi}{\epsilon kT} &\end{aligned}\quad (59.5)$$

In order to solve this equation, it is assumed that the ratio of electric energy to thermal energy ( $e\psi/kT$ ) is  $\ll 1$ . If this is true,  $\sinh e\psi/kT$  may be replaced by the argument,  $e\psi/kT$ . When  $ze\psi/kT < 0.25$ , the error in using the last form of Equation (59.5) is less than 1 per cent. The coefficient of  $\psi$  in the simplified expression has the dimensions  $l^2$ , and replacing the coefficient with  $\kappa^2$  we may write

$$\nabla^2\psi = \kappa^2\psi \quad (59.6)$$

Expressing concentrations in  $c$  moles per liter, instead of  $n$  molecules per cubic centimeters (i.e.,  $c = 1000 n/N$ ), and remembering that  $\frac{1}{2}\sum c_i z_i^2$  is, by definition, the ionic strength  $\frac{1}{2}\Gamma$ , we have

$$\sqrt{\frac{8\pi N e^2}{1000 \epsilon k T} \frac{\Gamma}{2}} \quad (59.7)$$

The solution of Equation (59.6) depends on the shape of the charged interface or particle. For a plane, or a very large sphere, where  $x$  is the distance perpendicular to the surface, the equation reduces to

$$\frac{d^2\psi}{dx^2} = \kappa^2\psi \quad (59.8)$$

the solution of which is

$$\psi = A e^{-\kappa x} \quad (59.9)$$

where  $A$  is determined by the level chosen to represent the extreme inner face of the double layer, beyond which the ions of the double layer can not penetrate. Since the total charge of the diffuse layer just neutralizes the total charge on the inner layer, the net surface charge  $\sigma$  on this layer, is given by

$$\int_a^\infty \rho dx = \int_a^\infty \frac{\epsilon \kappa^2}{4\pi} A e^{-\kappa x} dx = \frac{\epsilon \kappa}{4\pi} A e^{-\kappa a} \quad (59.10)$$

$$\psi = \frac{4\pi\sigma}{\epsilon\kappa} e^{\kappa(a-x)} \quad (59.11)$$

where  $a$  may be the thickness of firmly adsorbed solvent on the surface in question or the radius of the ions of the diffuse layer. If the potential at the level  $a$  is called the zeta potential of the double-layer, i.e.,  $\psi_{x=a} = \zeta$ , then  $\zeta = 4\pi\sigma/\epsilon\kappa$ . Comparing this equation with those of Helmholtz and Smoluchowski shows that  $1/\kappa$  is equivalent to  $d$ , the thickness of the double layer. In other words,  $1/\kappa$  gives the thickness of the equivalent Helmholtz double-layer. The distance  $1/\kappa$  is that at which the potential falls to  $1/e$  of its value at  $x = a$ . In water at  $25^\circ$  the value of  $\kappa$  is  $0.33 \times 10^8 \sqrt{\Gamma/2} \text{ cm}^{-1}$ . A few values for  $1/\kappa$  are given below.

$\Gamma/2$	$1/\kappa$
1.0	3.0 Å
0.1	9.6
0.01	30.3
0.001	95.8

The value of  $\kappa$  expressed in Equation (59.7) is identical with that originally derived by Gouy, although the treatment given here is that of Debye and Hückel.<sup>2</sup> The advantage of the equation for the diffuse layer is that it shows that the thickness of the double-layer, and, therefore, the zeta potential vary with electrolyte concentration, even though the surface charge-density does not do so. Although it is strictly true only for plane surfaces, it should also be valid whenever radius of curvature is very large compared to  $1/\kappa$ .

For a spherical particle, the general solution of the basic Equation (59.8) is

$$\psi = \frac{Q e^{-\kappa x}}{\epsilon x} = \frac{4\pi r^2 \sigma e^{-\kappa x}}{\epsilon x} \quad (59.12)$$

where  $Q$  is the total charge on the sphere,  $\sigma$  is the surface charge-density, and  $x$  is measured from the center of the particle. It is assumed that the charge on the sphere is homogeneously distributed either throughout the sphere or upon the surface. If the charge is localized, the potential represents an average value. The potential at the surface of the sphere, which is assumed to coincide with the inner layer of the double-layer and to represent the potential of the double layer, is then

$$\frac{Q}{\epsilon r} e^{-\kappa r} = \frac{4\pi r \sigma}{\epsilon} e^{-\kappa r} \quad (59.13)$$

or, for dilute solutions and very small particle size, when

$$\zeta = \frac{Q}{\epsilon r} \frac{1}{(1 + \kappa r)} = \frac{4\pi \sigma r}{\epsilon(1 + \kappa r)}$$

which may be written

$$\zeta = \frac{Q}{\epsilon r} \frac{1/\kappa}{\left(\frac{1}{\kappa} + r\right)} = \frac{4\pi \sigma r}{\epsilon} \frac{1/\kappa}{\left(\frac{1}{\kappa} + r\right)} \quad (59.14)$$

<sup>2</sup> *Physikal. Z.*, **24**, 49, 185, 305, 575 (1923); **25**, 97 (1924)

For a small sphere, large enough, however, to obey Stokes's law,<sup>3</sup> the electrophoretic mobility  $u$  is

$$u = \frac{Q}{6\pi\eta r} \frac{1}{1 + \kappa r} \quad (59.15)$$

while for a very large sphere Smoluchowski's theory yields

$$u = \frac{Q}{4\pi\eta r} \frac{1}{1 + \kappa r} \quad (59.16)$$

It was Henry<sup>4</sup> who succeeded in clarifying the difference between the equation obtained by Hückel (59.15) and that obtained from the theory of Smoluchowski (59.16). He showed that Equation (59.15) is strictly valid only when the conductance of the particle is the same as that of the medium or when the particle is so small that no appreciable distortion of the external field occurs in the region of the double-layer. Since the conductance of the particle may generally be taken as zero, Hückel's equation may be applied only if the thickness of the double-layer is large compared to the radius of the spherical particle. If the thickness of the double-layer is smaller than the radius of the particle, the application of Smoluchowski's equation is justified for all particle shapes. For spheres in the intermediate range, Henry obtained the equation

$$u = \frac{\zeta\epsilon}{6\pi\eta} f(\kappa r) \quad (59.17)$$

where the function  $f(\kappa r)$  is 1.5, when the sphere is large compared with the thickness of its atmosphere (in agreement with Smoluchowski's equation) and is 1 when the sphere is small compared with the thickness of its atmosphere (in agreement with Hückel's equation). Values for the function  $f(\kappa r)$  have been tabulated by Gorin<sup>5</sup> and Mueller.<sup>6</sup>

In Henry's theory it is assumed that hydrodynamic inertia terms, electrical relaxation effects, and the slip of solvent on particles are negligible, and in addition that the size of the ions in the diffuse layer may be ignored and that  $e\psi/kT \ll 1$ . Because of these approximations the numerical factor may be even greater than 6.<sup>7</sup> A more exact theory would have to eliminate these assumptions and extend the theory to other shapes of particles. So far such attempts have not been successful because of mathematical difficulties, but Gorin<sup>8</sup> has derived a correction for the finite size of the ions in the atmosphere and obtained equations for circular disks and long cylinders.

<sup>3</sup> Hückel, *ibid.*, 25, 204 (1924).

<sup>4</sup> *Proc. Roy. Soc., A*, 133, 106 (1931).

<sup>5</sup> Abramson, Moyer, and Gorin, *Electrophoresis of Proteins* (New York: Reinhold Publishing Corp., 1942), p. 121.

<sup>6</sup> Cohn and Edsall, *Proteins, Amino Acids and Peptides as Ions and Dipolar Ions* (1943), p. 641.

<sup>7</sup> Mueller, *Symposium on Quantitative Biology*, 9 (1933).

<sup>8</sup> *J. Chem. Physics*, 7, 405 (1939).

No discussion of the problem of the electric double layer would be complete without mention of the work of Stern.<sup>9</sup> He has modified the model underlying the theory for a solid wall by dividing the liquid charge into two parts, a layer of ions adsorbed to the wall and a diffuse space charge. The distribution equilibrium of charge between the two layers is calculated in much the same way as one would derive an adsorption isotherm. It is a realistic approach to a difficult problem.

Since electrophoresis has become an extremely important and popular method for studying the electrical properties of proteins, it will be described in some detail.

(60) **Electrophoresis:**<sup>1</sup> The movement of colloidal particles with respect to the dispersion medium under the influence of an electric field may be studied by the methods employed for the determination of ionic mobilities in general, the moving boundary method and Hittorf's transference method, or in the case of larger particles by the direct microscopic or ultramicroscopic observation of the motion of single particles. The microscopic method has been useful in studying cells and purified proteins adsorbed on microscopically visible colloidion or quartz particles. Since the particles under observation are usually in a thin cell, a correction must be made for an independent and superimposed electroosmotic effect due to the electric double-layer at the walls of the containing cell which causes the measured mobilities to change markedly with the distance of the particles from the walls. The microscopic method described in detail by Abramson, Moyer, and Gorin,<sup>2</sup> is not useful in studying mixtures or preparing samples of purified protein, and the main emphasis will be placed on the moving boundary method.

The early developments of the moving boundary method have been reviewed elsewhere,<sup>3</sup> It is largely the more recent improvements introduced by Tiselius<sup>4</sup> which have made electrophoresis a powerful tool of investigation, particularly of the proteins. These improvements and their subsequent development are described below.

(1) While earlier investigators had applied the fluorescence or absorption of ultraviolet light by the protein to locate the position of the boundaries, Tiselius adapted the Foucault-Toepler schlieren effect.<sup>5</sup> Even more precise location of the moving boundaries and measurement of the refractive index gradient through the boundary has been made possible by the methods men-

<sup>9</sup> *Z. Elektrochem.*, **30**, 508 (1924).

<sup>1</sup> For reviews, see Tiselius, *The Harvey Lectures*, **35**, 37 (1939-40); Longworth and MacInnes, *Chem. Rev.*, **24**, 271 (1939); Symposium on Electrophoresis, *Ann. N. Y. Acad. Sci.*, **39**, 107-212 (1939); Longworth, *Chem. Rev.*, **30**, 323 (1942); Abramson, Moyer, and Gorin, *op. cit.*; MacInnes and Longworth, in Alexander, *Colloid Chemistry* (1944), Vol. 5, p. 387; Alberty, *J. Chem. Ed.*, **25**, 426, 619 (1948).

<sup>2</sup> *Op. cit.*

<sup>3</sup> Tiselius, *The Moving Boundary Method of Studying the Electrophoresis of Proteins*, Diss., Upsala (1930); Svedberg, *Colloid Chemistry* (2d ed.; 1928), p. 225.

<sup>4</sup> *Trans. Faraday Soc.*, **33**, 524 (1937).

<sup>5</sup> *Ibid.*

tioned in Section 10 for measuring refractive index gradients. The schlieren "photographs" obtained with these optical systems are plots of refractive index gradient against vertical distance in the electrophoresis cell and may be used to determine the concentrations of the various components as well as their mobilities. The relative concentration of a component is simply the ratio of its area in the pattern to the total area of the moving boundaries.

(2) Protein boundaries are easily disturbed during electrophoresis by convection currents caused by temperature gradients through the cell resulting from electrical heating. The temperature gradient through the electrophoresis cell can be reduced by using flattened cells, and Tiselius showed that the consequent density gradient may be minimized by carrying out the experiment near the temperature of maximum density of the buffer solution. For this reason thermostats for electrophoresis are kept at about 1°C.

(3) The usual form of the modern electrophoresis apparatus is shown in Fig. 35. The electrophoresis cell of U-shape is made in three sections, and the boundaries move in the two limbs which have internal dimensions of about  $85 \times 25 \times 3$  mm and optical surfaces on front and back. The initial boundaries between colloid solution and buffer are formed by "shearing," and compensated into the optical section. Silver-silver chloride electrodes in concentrated sodium chloride solution are used, so that no gas is formed during electrolysis, and the large electrode vessels serve to prevent the products of electrolysis from reaching the cell.

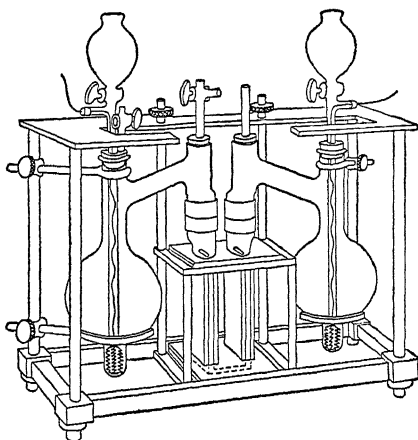


FIG. 35. Electrophoresis Apparatus.

The ideal limiting case in electrophoresis of colloids is that in which the solution below the initially sharp boundary contains a low concentration of colloidal species in a large excess of buffer ions, whereas only the buffer ions are present in the upper phase and at the same concentrations. The dominant species, the buffer ions, then insure throughout the boundary system a uniform electric field, pH, and salt concentration in which the colloid ions may move. As the electrophoresis is continued each colloidal species forms a separate moving boundary in which its concentration varies from a constant value below the boundary to zero above. In the ideal case there are no superimposed concentration gradients caused by other ions, and so the area of the corresponding peak in the plot of refractive-index gradient against position in the cell is a direct measure of the concentration of that species. In this ideal case the pattern obtained from the limb of the U-tube in which the boundaries are

descending is a mirror image of that obtained from the limb of the U-tube in which the boundaries are ascending. However, experimentally the ascending and descending patterns are not enantiographic as illustrated by Fig. 36 which is the electrophoresis pattern of normal human plasma. The following deviations from ideality may be observed: (1) The distances moved by the protein boundaries are greater in the ascending limb than in the descending one. (2)

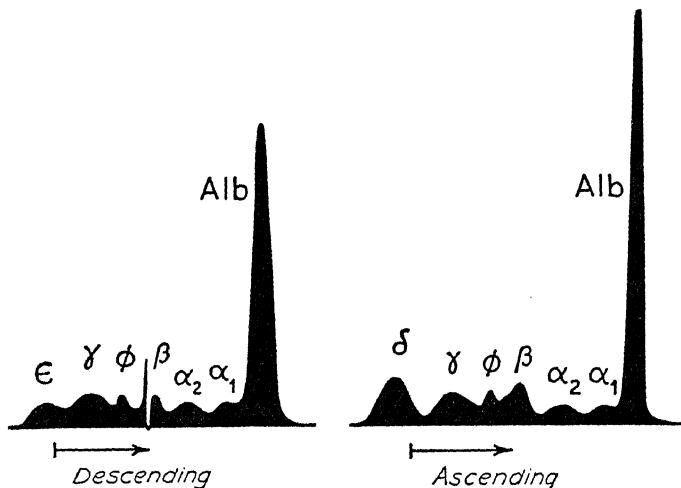


Fig. 36. Electrophoresis Pattern of Normal Human Plasma in 0.10 Ionic Strength Diethylbarbiturate Buffer. The schlieren photograph was taken after 2 hours at a potential gradient of 6 volts/cm.

The rising albumin boundary is sharper than the descending albumin boundary. (3) There are protein ( $\delta$ ) and buffer ( $\epsilon$ ) concentration boundaries which do not correspond to additional protein components. (4) The total areas of the ascending and descending patterns are equal, but the area under the albumin peak, for example, is smaller in the ascending pattern than in the descending pattern. (5) The concentration distribution in the boundaries is not, in general, symmetrical about the maximum ordinate as might be expected if the boundaries were spread by diffusion alone. (6) The "apparent analysis" obtained by assuming the absence of superimposed gradients varies with ionic strength at constant pH and also somewhat with the composition of the buffer used.

These electrophoretic anomalies are a result of the fact that there are small gradients of conductivity, pH, and protein concentration across the moving boundaries in addition to the gradient of the protein constituent which disappears in the boundary. In the usual analytical electrophoresis experiment the analysis, both for protein compositions and electrophoretic mobilities, is calculated from the pattern ignoring these anomalies. The electrophoretic mobility  $u$  introduced in Equation (57.1) is the distance moved per second in a

1 volt/cm electric field by an average particle in the body of the colloid solution. It may be calculated most directly on the descending side by

$$u = v\lambda_P \quad (60.1)$$

where  $v$  is the volume (ml) moved through by the colloid boundary (corrected for the displacement the solvent experiences as a result of electrolysis) per coulomb and  $\lambda_P$  is the specific conductance of the protein solution. While this equation holds accurately only for the fastest component in a mixture, "mobilities" for slower components may also be computed from the descending pattern and are useful for identification although, quantitatively, they are subject to small errors. The computation of mobilities from data for the ascending boundary is complicated by the change of protein concentration at the  $\delta$  boundary. The mobilities of colloids are in general somewhat lower than the mobility of inorganic ions and the range in mobilities is shown in Table XXII.

TABLE XXII  
IONIC MOBILITIES IN CM<sup>2</sup> SEC<sup>-1</sup> VOLT<sup>-1</sup> AT 0°C

Chloride ion (in 0.1 N NaCl)	- 37.2 × 10 <sup>-5</sup>
Sodium ion (in 0.1 N NaCl)	+ 22.1 × 10 <sup>-5</sup>
Acetate ion (in 0.1 N NaOAc)	- 17.3 × 10 <sup>-5</sup>
Diethylbarbiturate ion (in 0.1 N NaV)	- 10.3 × 10 <sup>-5</sup>
Nucleic acid, pH 7.0, $\Gamma/2 = 0.1$ (Phosphate buffer)	- 14.0 × 10 <sup>-5</sup>
Human serum albumin, pH 8.6, $\Gamma/2 = 0.1$ (NaV)	- 5.9 × 10 <sup>-5</sup>
Human serum gamma globulin, pH 8.6, $\Gamma/2 = 0.1$ (NaV)	- 1.0 × 10 <sup>-5</sup>

Although the qualitative aspects of these deviations from enantiography are understood and simple relations are obtained for the three ion systems,<sup>6</sup> the theory has not yet reached the point that accurate mobilities and concentrations of ions in the protein solution may be calculated directly from the boundary pattern in more complicated systems.

The relationship between the displacement of a single moving boundary and the concentration and mobilities of the ion species in the homogeneous solutions on either side of the boundary is of fundamental importance and is referred to as the moving boundary equation.<sup>7</sup>

This equation represents the law of conservation of mass for a moving boundary system and may be derived in a form applicable to both strong and weak electrolytes as follows.

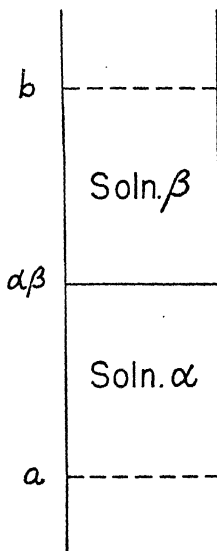
In the system illustrated in Fig. 37, the  $\alpha\beta$  boundary moves into the  $\beta$  solution, and planes  $a$  and  $b$  are fixed with respect to the solvent and are located at a sufficient distance from the moving boundary that the boundary does not reach them during the passage of one coulomb. If the  $j$ th constituent of a

<sup>6</sup> Longworth and MacInnes, *J. Am. Chem. Soc.*, **62**, 705 (1940); Svensson, *Arkiv Kemi Mineral. Geol.*, **22A**, No. 10, 1 (1946); Longworth, *J. Phys. Chem.*, **51**, 171 (1947).

<sup>7</sup> Weber, *Sitzungsber. Akad. Wissensch.*, Berlin, 936 (1897); Longworth, *J. Am. Chem. Soc.*, **67**, 1109 (1945); Svensson, *Arkiv Kemi Mineral. Geol.*, **17A**, No. 14, 1 (1943); Svensson, *Acta Chem. Scand.*, **2**, 855 (1948); Alberty, *J. Am. Chem. Soc.*, **72**, 2361 (1950).



solution consists of several forms which are in equilibrium having concentrations  $c_1, c_2, \dots, c_n$  gram formula weights per ml. and mobilities  $u_1, u_2, \dots, u_n$ , the net gain in the amount of the  $j$ th constituent between planes  $a$  and  $b$  per coulomb is  $v^{\alpha\beta}[(c_1^\alpha + c_2^\alpha + \dots + c_n^\alpha) - (c_1^\beta + c_2^\beta + \dots + c_n^\beta)]$ . Calculated in another way, the gain in amount of the  $j$ th constituent between planes



$a$  and  $b$  is the difference between the amount migrating into the volume under consideration at  $a$  and out at  $b$ . The transport of ion 1 through plane  $a$  is  $u_1^\alpha c_1^\alpha / \kappa^\alpha$  gram formula weights per coulomb, and so the transport of the  $j$ th constituent through plane  $a$  is  $(u_1^\alpha c_1^\alpha + u_2^\alpha c_2^\alpha + \dots + u_n^\alpha c_n^\alpha) / \kappa^\alpha$  and through plane  $b$  is  $(u_1^\beta c_1^\beta + u_2^\beta c_2^\beta + \dots + u_n^\beta c_n^\beta) / \kappa^\beta$  gram formula weights per coulomb. The gain in amount of the  $j$ th constituent between planes  $a$  and  $b$  as expressed in terms of the mobility must be equal to the gain expressed in terms of the displacement of the moving boundary, therefore

$$\frac{\bar{u}_j^\alpha \bar{c}_j^\alpha}{\kappa^\alpha} - \frac{\bar{u}_j^\beta \bar{c}_j^\beta}{\kappa^\beta} = v^{\alpha\beta}(\bar{c}_j^\alpha - \bar{c}_j^\beta) \quad (60.2)$$

where  $\bar{c}$  is the concentration of the  $j$ th constituent  $(c_1 + c_2 + \dots + c_n)$  and  $\bar{u}$  is the constituent mobility  $(u_1 c_1 + u_2 c_2 + \dots + u_n c_n) / \bar{c}$ .

Dole<sup>3</sup> developed a solution for the moving boundary equation for strong electrolytes assuming the relative ionic mobilities constant throughout the system. The displacements of the boundaries and the composition of the solutions formed by their separation are computed from the relative mobilities and concentrations of the two solutions forming the original boundary. The inverse problem of computing the mobilities and concentrations of the ions in the original solutions from the boundary pattern is, however, the one that arises in the electrophoretic analysis of protein mixtures and has not yet been solved. According to Dole's theory the interface between two solutions which together contain  $n$  ions will in general form  $n - 1$  boundaries under the influence of an electric field. If the system contains  $p$  anions and  $q$  cations, there will generally be  $p - 1$  boundaries with negative velocities and  $q - 1$  with positive velocities. The moving boundary equation holds for each boundary, and the  $V\sigma$  products for the various boundaries, where  $V$  is the volume in liters through which the boundary moves per 96,500 coulombs and  $\sigma$  is the relative conductance ( $\Sigma rc$ , where  $r$  is relative mobility and  $c$  is concentration in gram equivalents per liter), are the solutions for polynomials involving the known relative mobilities and

<sup>3</sup> *J. Am. Chem. Soc.*, **67**, 1119 (1945).

concentrations, viz.,

$$\begin{aligned} \frac{r_1 - r_n}{r_1 - x} C_1^\alpha + \frac{r_2 - r_n}{r_2 - x} C_2^\alpha + \dots + \frac{r_{n-1} - r_n}{r_{n-1} - x} C_{n-1}^\alpha &= 0 \\ \frac{r_1 - r_n}{r_1 - x} C_1^\eta + \frac{r_2 - r_n}{r_2 - x} C_2^\eta + \dots + \frac{r_{n-1} - r_n}{r_{n-1} - x} C_{n-1}^\eta &= 0 \end{aligned} \quad (60.3)$$

Here  $r_n$  is the relative mobility of the positive ion with the greatest mobility. The roots of each polynomial, if ordered from the extreme negative to the most positive, correspond to the appropriate set of  $V\sigma$  products, similarly ordered. If, as in the general case for protein, an ion disappears in a moving boundary the concentration of the other species may be calculated from

$$c_{j\beta} = \frac{(V^{\alpha\beta}\sigma^\beta)(r_g - r_j)}{r_g(V^{\alpha\beta} - r_j)} c_{j\alpha} \quad (60.4)$$

where  $r_g$  is the relative mobility of the ion which disappears in the boundary.

Although this theory is applicable to strong electrolytes only insofar as the presence of the buffer electrolytes insures a uniform pH and hence a constant relative mobility for the colloid ion, a number of important conclusions results. (1) The mobility for an ion may be calculated directly from the boundary velocity only when it disappears in the boundary. (2) At a stationary boundary, as the  $\delta$  and  $\epsilon$  boundaries in Fig. 36, all ion species must be present in the same relative proportion in the solutions on either side. (3) At a moving boundary, no two ion species having different mobilities can remain in the same relative proportions in the solutions on either side. (4) In the descending pattern the refractive-index increment given by the leading ion is enlarged by slower surrounding ions of the same charge, and in the ascending pattern the refractive-index increment given by the slower ion is decreased by faster surrounding ions of the same charge. Thus, the apparent composition determined from the electrophoresis pattern yields too great a value for the more rapid component in both limbs of the U-tube. The true composition of a protein mixture may be obtained by extrapolation of the apparent composition either to zero protein concentration at constant ionic strength or to infinite salt concentration at constant protein concentration.<sup>9</sup>

The electrophoretic mobility of colloids varies with pH, ionic strength, and the nature of the specific ions present. It was recognized early that most colloids move toward the cathode in strongly acid solutions and toward the anode in strongly alkaline solutions. At some intermediate pH the colloidal particle does not move with respect to the solvent under the influence of an electric field. Under these conditions the colloid is said to be isoelectric.<sup>10</sup> The isoelectric point is an important characteristic of a colloidal electrolyte because it is the condition under which many of the physical properties of the colloid are

<sup>9</sup> Svensson, *Ark. Kemi. Mineral. Geol.*, 17A, No. 14, p. 1 (1943); Longworth, *J. Phys. Colloid Chem.*, 51, 171 (1947).

<sup>10</sup> Hardy, *J. Physiol.*, 33, 251 (1905).

at a minimum (osmotic pressure, electrical conductivity, swelling, viscosity, solubility). Since the isoelectric point depends upon the ionic strength and the salts present, because of the specificity of salt-colloid interactions, it is necessary to specify the salts present and their concentrations as well as the pH in giving an isoelectric point. Figure 38 shows that by plotting the valence of the protein as ordinates and shifting the scale so that  $z = 0$  at pH 4.58, the isoelectric point of ovalbumin at  $\Gamma/2 = 0.10$ , the electrophoretic mobilities parallel the titration curve closely over the entire pH range.

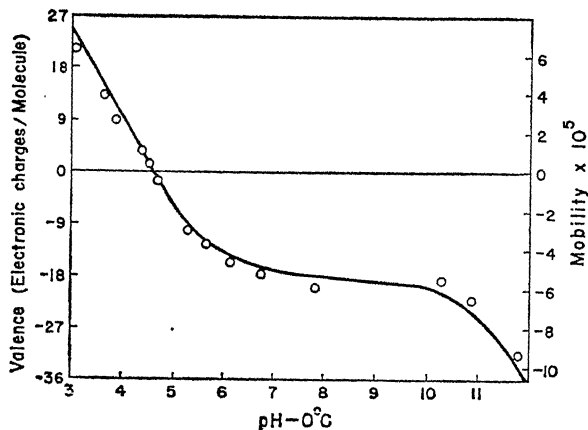


Fig. 38. Electrophoretic Mobility (open circles) and Valence (solid line) of crystallized Ovalbumin at 0.10 Ionic Strength. (Adapted from Longworth, *loc. cit.*)

In the case of proteins or other colloidal electrolytes it is useful to use the term isoionic point, which was first introduced by Sørensen, Linderstrom-Lang, and Lund.<sup>11</sup> Following Scatchard<sup>12</sup> the isoionic point may be defined in terms of isoionic material. Isoionic material is one which gives no non-colloidal ions other than hydrogen and hydroxyl. Operationally we may define the isoionic material as the limit approached by successful electrodialysis. The isoionic point is defined as the pH of a solution of the isoionic material in water, or in a solution of another solute which does not produce hydrogen or hydroxyl ions when dissolved in water alone. The shift of isoionic point with salt concentration shows marked specificity, and the effect follows a typical Hofmeister series.

A very important application of electrophoresis has been the analysis of protein mixtures, e.g., those occurring in natural fluids, such as plasma, and those resulting during the course of fractionations to obtain purified components. For example, the electrophoretic pattern of normal human plasma (Fig. 36) shows peaks for albumin, for globulins ( $\alpha_1$ ,  $\alpha_2$ ,  $\beta$ ,  $\gamma$ ), and for fibrinogen ( $\phi$ ).

<sup>11</sup> *J. Gen. Physiol.*, 8, 543 (1927). See also Sørensen, Høyrup, Hempel, and Palitzsch, *C. r. Laboratoire Carlsberg*, 12, 149 (1917).

<sup>12</sup> *J. Phys. Colloid Chem.*, 53, 88 (1949).

The analysis is obtained by constructing symmetrical and approximately Gaussian curves for each of the components so that the ordinates add up to give the experimental gradient curve. The areas under these curves are taken as proportional to the relative amounts of the various proteins present. However, these electrophoretic components of plasma are not necessarily homogeneous with respect to size, shape or isoelectric point, but correspond to "families" of closely related proteins. Alcohol fractionation<sup>13</sup> of the plasma proteins, using electrophoresis for analysis of the fractions, has resulted in the isolation of some of these components so that their functions may be studied. Many pathological conditions are accompanied by marked and distinctive changes in the plasma pattern. Electrophoresis may be used for the isolation of a protein from a mixture so that it may be further studied. This is simple only if the desired protein is the slowest or fastest component in the mixture. Determination of electrophoretic mobility as a function of pH and ionic strength yields the isoionic point and is also useful in characterization. If a colloid shows only one moving boundary in electrophoresis at various hydrogen ion concentrations and ionic strengths and the boundary spreads no faster than expected for diffusion while in an electric field under conditions such that convection spreading and that caused by gradients in the field through the boundary are negligible, the colloid may be said to be electrophoretically homogeneous.<sup>14</sup> Small samples of proteins which are difficult to separate by other methods may be isolated in electrophoretic experiments. The various types of apparatus used for this purpose have been described by Svensson.<sup>15</sup>

An ingenious electrophoresis-convection method for the separation of protein fractions has been devised by Kirkwood *et al.*<sup>16</sup>

**(61) Other Experimental Electrokinetic Methods:** It is difficult to obtain precise quantitative data by the other electrokinetic methods and since the other methods have not been developed to the extent of electrophoresis, the results often are controversial.

**Streaming Potential:** Streaming potential measurements have some advantages over electroosmosis and sedimentation potential measurements because they are easier to control experimentally. The potential difference between the two ends of a capillary tube or porous plug through which liquid is being forced may be measured with a quadrant electrometer or a vacuum-tube potentiometer. The streaming potential is independent of the length and size of the capillary. Streaming potential measurements have been carried out on a number of substances.<sup>1</sup>

<sup>13</sup> Cohn, *Trans. & Studies Coll. Physicians Phila.*, Series 4, 10, 149 (1942); *Proc. Am. Phil. Soc.*, 88, 159 (1944); Cohn, *et al.*, *J. Am. Chem. Soc.*, 68, 459 (1946).

<sup>14</sup> Alberty, *J. Am. Chem. Soc.*, 70, 1675 (1948); Alberty, Anderson, Williams, *J. Phys. Coll. Chem.*, 52, 217 (1948).

<sup>15</sup> *Advances in Protein Chemistry* (New York: Academic Press, 1948), Vol. IV.

<sup>16</sup> Kirkwood, *J. Chem. Phys.*, 9, 878 (1941); *J. Am. Chem. Soc.*, 68, 181 (1946); 71, 1609, 2867 (1949).

<sup>1</sup> Briggs, *J. Phys. Chem.*, 32, 641 (1928); Komagata, *Res. Electrotech. Lab. Tokyo*, No. 362, 1934; Bull, *J. Am. Chem. Soc.*, 57, 259 (1935); Bull and Moyer, *J. Phys. Chem.*, 40, 9 (1936);

**Electroosmosis:** In the early experimental studies on electroosmosis <sup>2</sup> Wiedemann demonstrated in experiments with clay diaphragms, that the amount of water transported is proportional to the electric current. A convenient arrangement for measuring the rate of electroosmotic flow <sup>3</sup> is to follow the rate of motion of an air bubble through a calibrated capillary shunted across the membrane or porous plug between the electrodes.

**Sedimentation Potential (Dorn effect):** <sup>4</sup> Rather large potential differences may be established by falling powders. For example, quartz powder falling through toluene may produce potential differences of the order of 100 volts between the top and bottom of a column. Although most of the work has been done in organic solvents, <sup>5</sup> Quist and Washburn <sup>6</sup> have obtained quantitative information on aqueous solutions.

In addition to the four electrokinetic methods, information concerning the nature of the electrical double layer may be obtained from a study of the dependence of interfacial tension upon the electrical potential across the interface. In the Lippmann <sup>7</sup> capillary electrometer the mercury-aqueous solution interfacial tension is found to be a function of the potential difference and the solutes present in the aqueous phase. <sup>8</sup> Gibbs <sup>9</sup> has shown that the decrease  $d\gamma$  in interfacial tension caused by the presence of either positive or negative charges on the surface should be given by

$$d\gamma = e dV - \sum \Gamma_i d\mu_i \quad (61.5)$$

where  $V$  is the potential difference across the interface,  $e$  is the quantity of charge which must be transferred across the interface in order to keep  $V$  constant when the interfacial area is increased by unity, and  $\Gamma_i$  and  $\mu_i$  are the excess surface concentration and chemical potential of the  $i$ th component. This subject has been reviewed by Grahame. <sup>10</sup>

## PREPARATION AND STABILITY OF COLLOIDAL SYSTEMS

(62) **Intrinsic Colloids:** The preparation <sup>1</sup> of a colloidal solution involves the formation of submicroscopic or microscopic particles containing a few

Bikerman, *ibid.*, **46**, 724 (1942); Laufer and Gortner, *ibid.*, **42**, 641 (1938); Reyerson, Koltzoff, and Coal, *J. Phys. Colloid. Chem.*, **51**, 321 (1947).

<sup>2</sup> Reuss, *Mém. Soc. Imp. Naturalistes Moscou*, **2**, 327 (1809); Wiedemann, *Ann. Physik*, **87**, 321 (1852); **99**, 177 (1856); Quincke, *ibid.*, **113**, 513 (1861).

<sup>3</sup> Strickler and Mathews, *J. Am. Chem. Soc.*, **44**, 647 (1922); Fairbrother and Balkin, *J. Chem. Soc.*, 387 (1931).

<sup>4</sup> Dorn, *Ann. Physik*, **10**, 46 (1880).

<sup>5</sup> Stock, *Anz. Akad. Wiss. Krakau*, 131 (1905); 95 (1914).

<sup>6</sup> *J. Am. Chem. Soc.*, **62**, 3169 (1940).

<sup>7</sup> *Ann. Chim. Phys.*, [5], **5**, 494 (1875).

<sup>8</sup> Frumkin, *Colloid Symposium Annual* (1930), p. 89.

<sup>9</sup> Gibbs, *Collected Works* (1928), Vol. I, p. 230.

<sup>10</sup> *Chem. Rev.*, **41**, 441 (1947).

<sup>1</sup> This subject has been discussed very thoroughly by Svedberg, *Die Methoden zur Herstellung kolloider Lösungen anorganischer Stoffe* (Dresden: Steinkopf, 1909); *The Formation of*

hundred or more atoms, i.e., having a diameter of about  $1\text{ m}\mu$  or greater, and the dispersion of these particles in a liquid medium.<sup>2</sup>

If single molecules have these dimensions,<sup>3</sup> their solutions possess colloidal properties; they are inherently colloids or "natural colloids." In such cases it is sufficient to bring the material to be dispersed into contact with a sufficiently good solvent, whereupon the molecules spontaneously pass into solution, although usually somewhat slowly on account of the high cohesion and low diffusivity of large molecules. The particles in aqueous solutions of egg albumin, hemoglobin, serum albumin, and some other proteins<sup>4</sup> appear to be single molecules, and the same may be true of "low-viscosity" cellulose, cellulose ethers and esters, rubber, agar, gums, polysaccharides, and various synthetic macromolecular polymers in suitable solvents. In the proteins named, the "molecules" may be essentially uniform in size, but this is by no means typical of either naturally-occurring or synthetic materials of high molecular weight. In addition, the colloid particles may not be single molecules in many cases, for there is equal, if not more, reason to expect association of the solute in macromolecular solutions than in solutions of small molecules. The relations between macromolecular particles and a dispersing medium are much the same as between small molecules and their solvent, and the macromolecular solutions also are apparently thermodynamically stable. Even molecules or ions of moderate size may spontaneously aggregate to particles that form thermodynamically stable colloidal solutions; the best known example is that of the soaps (page 668). Because of the affinity between the solvent and the solute, these colloidal solutions are said to be "lyophilic" in contrast to the "lyophobic" type.<sup>5</sup>

It has been remarked (page 513) that there has been recently developed a new chemistry of macromolecules. These substances are intrinsic colloids, being formed by a growth process, starting from small molecules with two or more combining groups. The macromolecules may be of natural or of synthetic origin. Among the former mention may be made of cellulose, starch and rubber, which, to a first approximation, contain single repeating groups just as do the simplest chemical types of high polymer. Often, however, better practical properties of finished material are obtained in co-polymers which are giant molecules with two or more different repeating groups, for instance butadiene and styrene in the rubber substitute GR-S. Proteins may be thought of as

*Colloids* (London: Churchill, 1921); *Colloid Chemistry* (2d ed.; 1928). See also Reitstötter, in Liesegang, *Kolloidchem. Technologie* (Dresden and Leipzig: Steinkopf, 1927), pp. 5, 57.

<sup>2</sup> Microscopic particles give obviously turbid suspensions when dispersed in a liquid of different refractive index and fairly quickly settle out under the influence of gravity unless their density is very near that of the dispersion medium. In acknowledgment of the usual connotation of "solution," the term "colloidal solution" is ordinarily restricted to dispersions of particles that are submicroscopic or almost so, i.e., less than  $0.5$  to  $1.0\text{ }\mu$  in diameter.

<sup>3</sup> Staudinger, *Ber.*, 59, 3019 (1926), refers to such giant molecules as "macromolecules."

<sup>4</sup> Svedberg and Pedersen, *The Ultracentrifuge* (Oxford: 1940), p. 1598.

<sup>5</sup> Perrin, *J. chim. Phys.*, 3, 84 (1905); Freundlich, *Colloid and Capillary Chemistry* (1926), p. 362.

being natural macromolecules, but they have a number of different amino-acid building units. The fundamental principles of condensation polymerization have been described by Flory.<sup>6</sup> In this article and in a number of other places<sup>7</sup> lists and formulae of representative synthetic polymers are tabulated.

*Polymers:* Organic macromolecules may be divided into two main types:

1. Linear or long chain polymers,
2. Three dimensional networks or space polymers.

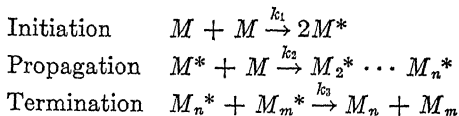
The members of each of these groups may be further classified according as to whether they were formed by (a) condensation reactions, or (b) addition reactions.

Linear polymers result from reactants which are exclusively bifunctional, e.g.,  $\omega$ -hydroxy-carboxylic acid, or styrene; while the three-dimensional networks or space polymers are formed when one or more of the reactants are trifunctional, tetrafunctional etc., e.g., glycerol, or divinyl benzene. The linear polymers being of finite molecular weight are usually soluble in a suitable solvent, and are often fusible on heating. The three dimensional networks on the other hand may be of infinite molecular weight and hence may swell when treated with "solvents" but will not dissolve; they are infusible on heating without chemical decomposition.

Condensation polymers, which, as we have indicated, may be linear or three dimensional, are formed when water (or other small molecule) is split out between functional groups such as  $-\text{OH}$  and  $-\text{COOH}$ , or  $-\text{NH}_2$  and  $-\text{COOH}$ , yielding polyesters and polyamides, respectively. Flory has carried out experimental studies on the rates of esterification of mono- and polyfunctional reactants and has shown that the functional group reacts almost independently of the length of the chain to which it is attached. Thus, a polycondensation reaction can be characterized by a single rate constant.<sup>8</sup>

Since in this type of polymerization reaction may occur between functional groups on chains of all lengths it follows that the chain length or molecular weight of the final polymer depends on the extent to which the reaction has been allowed to proceed.

Addition polymerization of the vinyl type is of a much more complicated nature. In the simplified case there are three fundamental steps, viz., chain initiation, propagation and termination;<sup>9,10</sup> and associated with each step is a specific reaction rate constant.



<sup>6</sup> *Chem. Rev.*, **39**, 137 (1946).

<sup>7</sup> Powers, *News Ed. Ind. Eng. Chem.*, **22**, 1992 (1944); Marvel and Horning, in Gilman, *Organic Chemistry* (New York: John Wiley & Sons., 1943), Vol. II.

<sup>8</sup> Flory, *J. Am. Chem. Soc.*, **61**, 3334 (1939).

<sup>9</sup> Staudinger and Frost, *Ber.*, **68**, 2351 (1935).

<sup>10</sup> Flory, *J. Am. Chem. Soc.*, **59**, 241 (1937).

In the initiation reaction the active centers ( $M^*$ ) may be formed either by monomer collision, catalyst decomposition or by photoactivation. Chain growth then proceeds by way of a very rapid free radical chain mechanism involving monomer addition only; and termination of chain growth occurs when the active center is destroyed. Unlike the condensation reaction there is no gradual lengthening of the polymer molecules, as the reaction proceeds, each grows to its full size extremely rapidly and then stops. Thus the molecular weight of the polymer product is independent of the extent of the reaction, and is rather a function of the reaction rate constants of the fundamental steps involved and the relative concentrations of monomer and catalyst.

Of considerable importance in the study of such polymerization reactions is the investigation of the average molecular weight and the molecular weight distribution of the products formed. The theoretical distribution of molecular sizes is most readily obtained for a polymer of the linear condensation type, e.g., an  $\omega$ -hydroxy carboxylic acid. Two different methods are available for obtaining this result, the statistical<sup>11</sup> and the kinetic<sup>12</sup> approaches. Both methods depend for their simplicity on the experimental fact previously mentioned that the reactivity of the functional groups is independent of the lengths of the chains to which they are attached. If in the statistical method we let  $p$  represent the probability that at a given time a  $-\text{COOH}$  group picked at random has reacted, which is equivalent to saying that a fraction  $p$  of the total  $-\text{COOH}$  groups has reacted, we find that the total number of  $x$ -mers is given by  $N_x = N_0(1 - p)^2 p^{x-1}$  (where  $N_0$  is the number of monomer units in the original system), and that the weight fraction of an  $x$ -mer is given by

$$w_x = x \frac{N_x}{N_0} = x(1 - p)^2 p^{x-1} \quad (62.1)$$

From these equations the number fraction (mole fraction) and weight fraction distribution curves may be computed. Also, the average molecular sizes may be determined and are found to be:

$$\overline{M}_n = M_0 \frac{1}{1 - p} \quad (\text{number average}) \quad (62.2)$$

$$\overline{M}_w = M_0 \frac{1 + p}{1 - p} \quad (\text{weight average}) \quad (62.3)$$

It is thus seen that as the extent of reaction tends to completion, i.e., as  $p$  tends to 1, the ratio  $\overline{M}_w/\overline{M}_n$  approaches 2.

The kinetic method, which is based on the integration of a set of differential equations describing the rates of formation and destruction of the molecules of all sizes yields the same results.

<sup>11</sup> Flory, *J. Am. Chem. Soc.*, **58**, 2877 (1936).

<sup>12</sup> Mark, *The Chemistry of Large Molecules* (New York: Interscience Publishers, 1943), chap. 1.



The determination of the molecular size distribution for addition polymers of the vinyl type is much more complicated than that for condensation systems. The kinetic method has been applied in a general way<sup>13</sup> to such systems. The distributions are shown to be functions of the reaction rates of the various steps involved in the polymer formation.

Until recently the experimental evaluation of the molecular weight distribution of linear polymers has been a tedious process, involving exhaustive fractionation followed by molecular weight determinations on each of the fractions; and as a result the procedure has been carried through for very few polymers. However, work by Wales, *et al.*<sup>14</sup> with polystyrene has shown that sedimentation equilibrium studies on the unfractionated polymer are capable of yielding accurate data for the molecular weight distribution and the various molecular weights.

Analysis of the constitution and molecular weight distribution of three-dimensional condensation polymers is much more difficult. Among other things the problem is complicated by the appearance of gelation in the system. After such gelation there are two parts to the system, sol and gel, and as the curing process proceeds the former disappears as the latter increases in amount. Flory<sup>15</sup> and Stockmayer<sup>16</sup> have made definite progress by using the statistical method (as contrasted with the kinetic method). The polyfunctionality of the reacting monomer units leads to a molecular size distribution which is extremely broad compared to that of linear polymers. In the bifunctional case a linear molecule possesses two end groups irrespective of size. In the trifunctional case the larger the molecule the more end groups it carries. Thus, tetramers each have six end groups and an  $x$ -mer has  $(x + 2)$  end groups since it contains  $3x$  groups in all and  $2(x - 1)$  groups have been used to form bonds. In this way the larger molecules have a better chance for growth than do smaller ones, and a broader distribution is to be expected.

For the weight fraction  $w_x$  of polymer containing  $x$  units and excluding ring formation we may write

$$\text{Bifunctional Case} \quad w_x = x(1 - p)^2 p^{x-1} \quad (f = 2) \quad (62.4)$$

$$\text{Trifunctional Case} \quad w_x = \frac{3(2x)}{(x - 1)!(x + 2)!} p^{x-1}(1 - p)^{x+2} \quad (f = 3) \quad (62.5)$$

$$\text{Tetrafunctional Case} \quad w_x = \frac{4(3x)!}{(x - 1)!(2x + 2)!} p^{x-1}(1 - p)^{2x+2} \quad (f = 4) \quad (62.6)$$

<sup>13</sup> Ginell and Simha, paper presented at the *Am. Chem. Soc.* Meeting in Buffalo, September, 1942.

<sup>14</sup> Wales, Bender, Williams, and Ewart, *J. Chem. Phys.*, **14**, 5, 353 (1946); Wales, *J. Phys. Colloid Chem.*, **52**, 235 (1948); Wales, Williams, Thompson, and Ewart, *J. Phys. Colloid Chem.*, **52**, 984 (1948).

<sup>15</sup> *J. Am. Chem. Soc.*, **63**, 3083, 3091, 3096 (1941); *J. Phys. Chem.*, **46**, 132 (1942).

<sup>16</sup> *J. Chem. Physics*, **11**, 45 (1943); **12**, 125 (1944); **11**, 393 (1943).

In Fig. 39 we show three curves for the three cases,  $f = 2$ ,  $f = 3$ , and  $f = 4$ . These curves do not correspond to the same extent of reaction,  $p$ , but rather to the same number average degree of polymerization. If the number of functional groups per monomer unit is  $f$ , the number of bonds formed will be  $fN_0p/2$  and the number of molecules will be  $N = N_0 - \frac{fN_0p}{2}$ . Therefore,

$$DP_n = \frac{N_0}{N} = \left(1 - \frac{fp}{2}\right)^{-1} \quad (62.7)$$

The three curves are drawn for  $DP_n = 2$ , i.e.,  $p = \frac{1}{2}, \frac{1}{3}, \frac{1}{4}$ .

This figure, and others like it, shows that even when  $DP_n$  is small and although the majority of the molecules are still small, a few of the molecules are so huge that the weight distribution is spreading out toward successively higher values of  $x$ .

The ultimate effect of this trend toward unequal distribution is demonstrated by the expression for the weight average degree of polymerization.

$$\overline{DP}_w = \frac{\sum xw_x}{\sum w_x} = \frac{1+p}{1-(f-1)p}$$

According to this equation  $\overline{DP}_w$  becomes indefinite when  $p$  reaches a critical value. For one type of

monomer unit  $p_c = \frac{1}{f-1} = \frac{1}{2}$  for  $f = 3$  and  $\frac{1}{3}$  for  $f = 4$ . This critical

value for  $p$  has been associated with the setting or gel point of cross-linking resins. It depends only on the functionality of the monomers and is independent of temperature. This situation may be compared to the current theory of condensation of a vapor to a liquid.<sup>17</sup>

**Proteins:**<sup>18</sup> This large and important class of natural colloids consists of the most complicated of the organic macromolecules, being copolymers of some 15 to 20 constituents. The acidic and basic side chains of certain of the amino acids are not involved in peptide bonds and ionize and make the protein an amphoteric electrolyte. The number and nature of these dissociable groups may be studied by titration with strong acids and bases and by electrophoresis.

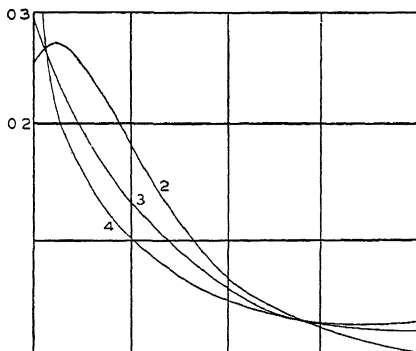


FIG. 39. Size Distribution Curves. Systems of 2-, 3- and 4- Functional Units when  $\overline{DP}_n = 2$ .

<sup>17</sup> Mayer and Mayer, *Statistical Mechanics* (New York: John Wiley and Sons, 1940).

<sup>18</sup> The colloid chemistry of the proteins is discussed in detail in Cohn and Edsall, *Proteins, Amino Acids, and Peptides* (1943); Schmidt, *Chemistry of the Amino Acids and Proteins* (Springfield, Ill.: Thomas, 1945); Loeb, *Proteins and the Theory of Colloidal Behavior* (2d ed.; New York: McGraw-Hill Book Co., Inc., 1924).

Proteins range from about 17,000 to 50,000,000 in molecular weight, but in contrast to the linear polymers the peptide chains are arranged in a rather specific and compact fashion. Globular proteins, isolated from natural fluids by methods which avoid denaturation, appear to be quite homogeneous on sedimentation and diffusion. A number of proteins have been crystallized and found to show constant solubility, suggesting the presence of a single chemical substance.

Variations in the solubility of proteins are conspicuous and are the basis for the usual classification. Constancy of solubility is one of the best criteria of the homogeneity of proteins.<sup>19</sup> The effects of salts on the solubility of different proteins at low ionic strength are, in general, greater and more specific than at the high ionic strengths employed in "salting-out." Salting-out for proteins, as for simpler molecules, even gases, depends largely upon the quantity of water displaced. By using alcohol, or other water miscible organic solvents, at low temperatures for protein fractionation, the electrolyte concentration may be maintained in the low range in which interactions with proteins depend largely upon the ionic strength and the specific electrochemical properties of the protein.<sup>20</sup> In this way human plasma has been separated into a number of fractions for medical applications.

The globular proteins, being soluble, can in some cases be obtained in crystalline form. X-ray studies with single crystals, which alone can be uniquely and properly interpreted, have been made on insulin by Crowfoot and Riley, on lactoglobulin by Crowfoot and Riley, on chymotrypsin by Bernal, *et al.* and by Perutz, on pepsin by Bernal and Crowfoot, on horse methaemoglobin by Bernal, *et al.* and by Perutz, and on excelsin by Astbury. The principal data obtained are collected in Table XXIII.

(63) **Extrinsic Colloids:** The colloidal state of subdivision for substances of small molecular weight, e.g., less than a few hundred, may be attained either by pulverizing gross masses or by condensing and precipitating particles from a supersaturated state of molecular subdivision (as from a vapor or a solution) under conditions that do not allow the immediate growth of the particles to macroscopic size. A finely-divided phase being thermodynamically unstable, these systems are "artificial colloids."

*Mechanical pulverization* has been used only in special cases for forming colloidal solutions. Even with the best commercial grinding equipment, it is a slow and expensive process to reduce a brittle substance into particles of microscopic dimensions, and malleable or rubbery substances can not be finely pulverized at all by grinding.<sup>1</sup> Long grinding preferably with a solid diluent which dissolves when the dispersion medium is added (von Weimarn's method),

<sup>19</sup> Northrop, *Crystalline Enzymes*, 2d ed. (New York: Columbia University Press, 1948).

<sup>20</sup> Cohn, Strong, Hughes, Mulford, Ashworth, Melin, and Taylor, *J. Am. Chem. Soc.*, **68**, 459 (1946).

<sup>1</sup> For a quantitative study of the dispersity obtainable with various commercial mills, see Andreasen, *Kolloidchem. Beih.*, **27**, 349 (1928).

TABLE XXIII  
MOLECULAR CHARACTERISTIC CONSTANTS OF CRYSTALLINE PROTEINS

Protein	Insulin <sup>(a)</sup>	Lactoglobulin <sup>(b)</sup>		Chymo- trypsin <sup>(c)</sup>	Horse methaemo- globin <sup>(d)</sup>	Tobacco seed globulin <sup>(e)</sup>	Excelsin <sup>(f)</sup>	Bushy stunt virus <sup>(g)</sup>
		Tabular	Needle					
Non X-ray molecular weight	35,100 40,900	37,900 41,800		41,000	66,700	300,000	294,000	7,600,000 8,800,000
$\alpha$ in Å.....	130	60	56	45	102	123	149	318
$b$ .....	74.8	63	56	62.5	51	123	86	318
$c$ .....	30.9	110	130	57.5	47	123	208.2	318
$\beta$ .....	90°	90°	90°	112°	130°	90°	90°	90°
$c \sin \beta$ .....	30.9	110	130	53.5	36	123	208.2	318
Vol. in Å <sup>3</sup> .....	298,000	416,000	408,000	151,000	188,000	1,850,000	2,670,000	32,000,000
$n$ .....	6	8	8	2	2	4	6	2
Volume per molecule.....	50,000	52,000	51,000	75,500	94,000	460,000	445,000	16,000,000
Density.....	1.315	1.30	1.30	1.31	1.270	1.287	1.317	1.35
Molecular weight.....	39,500	40,000	40,100	60,000	72,000	360,000	350,000	13,000,000
Molecular weight corrected for re- sidual water.....	37,400			54,000	66,700	322,000	305,800	I
Space group.....	R3	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	20	P2 <sub>1</sub>	C2	F	R3	
Smallest observed spacing.....	7	20	20	5	13			

(a) Crowfoot, *Proc. Roy. Soc. London*, A164, 580 (1938).(c) Crowfoot and Fankuchen, *Nature*, 141, 522 (1938).(b) Crowfoot and Riley, *Nature*, 141, 521 (1938).(e) Bernal, Fankuchen, and Perutz, *Nature*, 141, 523 (1938).(f) Bernal, Fankuchen, and Riley, *Nature*, 142, 1075 (1938).

(g) Perutz, Dissertation, Cambridge (1939).

does however yield an appreciable amount of submicroscopic particles.<sup>2</sup> Explosive gas-production within brittle solids is sometimes an efficient pulverizing agency.<sup>3</sup>

Liquids of fairly low viscosity may be finely pulverized by spraying or by violent agitation;<sup>4</sup> in either case unstable liquid films and threads form, which break up into drops under the influence of surface tension. The finest dispersions of one liquid into another are brought about by means of colloid mills<sup>5</sup> or homogenizers.<sup>6</sup> Although both phases are broken up in these cases, the final emulsion usually contains but one of the liquids in a dispersed state. The factors that determine which liquid remains subdivided are quite inadequately understood, but they include the volume ratio, the viscosities, densities, interfacial tensions, and the effect of added "emulsifiers" on the rates of coalescence of the two kinds of drops, the last being particularly important.<sup>7</sup> For instance, if equal volumes of water and a hydrocarbon containing a small amount of sodium oleate are shaken together an emulsion of oil in water is formed, whereas if calcium oleate is used the emulsion contains water particles suspended in oil.<sup>8</sup> Finely divided solids also function as emulsifying agents; certain ones, e.g., hydrous oxides, basic sulfates, clays, etc., yield oil-in-water emulsions, and others, e.g., carbon black, mercuric iodide, yield water-in-oil emulsions.<sup>9</sup> Many theories to interpret these differences have been proposed,<sup>10</sup> some of which will be referred to later (p. 687).

*Condensation methods* have usually been used in the formation of colloidal solutions. Table XXIV outlines and illustrates important methods for producing the supersaturated condition that precedes the condensation of molecules to form colloidal particles in an initially homogeneous phase.

The appearance of a new phase involves several steps: the aggregation of molecules to form nuclei, the growth of nuclei by deposition from the vapor or solution, the rearrangement of molecules if the precipitating material can be crystalline, the union of nuclei or particles to form aggregates, and re-solution

<sup>2</sup> von Weimarn, *Die Allgemeinheit des Kolloidzustandes*, p. 268; Utzino, in Alexander, *Colloid Chemistry*, Vol. I, chap. 39.

<sup>3</sup> Kohlschütter, *Die Erscheinungsformen der Materie* (Leipzig: Teubner, 1917), p. 143; Gibbs, *Clouds and Smokes* (London: Churchill, 1924), p. 11.

<sup>4</sup> An excellent survey of emulsions is given by Clayton *The Theory of Emulsions and Their Technical Application* (4th ed.; Philadelphia: Blakiston, 1943). An interesting application of spraying is Schoop's process for spraying metals, Turner and Budgen, *Metal Spraying* (London: Griffin, 1926).

<sup>5</sup> Travis, *Mechanochemistry and the Colloid Mill* (New York: Chem. Catalog Co., 1928).

<sup>6</sup> Clayton, *op. cit.* A dairy homogenizer is said to reduce the fat globules in milk to submicroscopic sizes.

<sup>7</sup> Stamm and Kraemer, *J. Phys. Chem.*, **30**, 992 (1926).

<sup>8</sup> Newman, *ibid.*, **18**, 34 (1914); Briggs and Schmidt, *ibid.*, **19**, 478 (1915); Clowes, *ibid.*, **20**, 407 (1916); Bhatnagar, *J. Chem. Soc.*, **117**, 542 (1920).

<sup>9</sup> Pickering, *J. Chem. Soc.*, **91**, 2001 (1907); *J. Soc. Chem. Ind.*, **29**, 128 (1910); Briggs, *loc. cit.*; *J. Ind. Eng. Chem.*, **13**, 1008 (1921); Moore, *J. Am. Chem. Soc.*, **41**, 940 (1919); Bhatnagar, *J. Chem. Soc.*, **119**, 1760 (1921); Bechhold, Dede, and Reiner, *Kolloid-Z.*, **28**, 6 (1921).

<sup>10</sup> Clayton, *op. cit.*

TABLE XXIV  
 FORMATION OF COLLOIDAL PARTICLES BY CONDENSATION PROCESSES<sup>1</sup>

Supersatd. state due to	Process and substances used	Investigators
Temp. change	Adiabatic expansion of condensible vapors: Water, benzene, alcohols. . . . .	Andrén
	Simultaneous solidification in high vacuum of mixed vapors of metals and hydrocarbons. . . . .	Polanyi and Bogdandy <sup>2</sup>
	Condensation in liquids of metals vaporized in an electric arc. . . . .	Bredig, Svedberg <sup>3</sup>
	Reduction in solubility by cooling: Pentane in water, sulfur in alcohol, etc. . . . .	von Weimarn
Solvent change	Excess water added to alc. solns. of fatty acids, dyes, sulfur, mastic, etc. . . . .	Svedberg, von Weimarn <sup>4</sup>
Chem. reaction giving new product of lower solu- bility	Reduction: Gold, silver, and other noble metals from their salts. . . . .	Faraday, Carey Lea, <i>et al.</i>
	Oxidation: $\text{H}_2\text{S} + \text{SO}_2 \rightarrow \text{S} + \text{thioacids}$ . . . . .	Odén
	Hydrolysis: Hydrous oxides from salts of metals. . .	Graham, <i>et al.</i>
	Double decomposition: Two soluble electrolytes, insoluble acids, hydroxides, oxides, sulfides, halides, and many other salts. . . . .	Graham, <i>et al.</i>
	Polymerization: Styrene, vinyl esters, acrylic-acid esters, etc. . . . .	Staudinger, <sup>5</sup> Carothers, <sup>6</sup> <i>et al.</i>

<sup>1</sup> Unless otherwise noted, references are given in Svedberg's treatises (footnote 3, p. 518).

<sup>2</sup> Brit. Pat., 269,586 (1928); *see also* Roginsky and Schalnikov, *Kolloid-Z.*, **43**, 67 (1927).

<sup>3</sup> Some pulverization may also occur.

<sup>4</sup> *Op. cit.*, p. 201.

<sup>5</sup> *Ber.*, **59**, 3019 (1926).

<sup>6</sup> Carothers, *High Polymers* (1940), Vol. I.

and re-deposition in such aggregates to form larger crystals. The dispersity and structure of the final particles depend upon the rates of these processes.

With increasing degree of supersaturation in a given system the rate of nuclear formation normally increases more rapidly than the rate of nuclear growth with the consequence that the dispersity of the final colloid also increases.<sup>11</sup> As a result of a great many experiments in liquid systems, von Weimarn drew the general semi-quantitative conclusion (von Weimarn's law of "corresponding crystallization conditions") that the rate of nuclear formation and the primary particle size in *any* precipitate is determined by a dispersity coefficient  $N$ , which is proportional to the relative supersaturation  $P/L$

<sup>11</sup> Von Weimarn, *Grundzüge der Dispersoid Chemie* (Dresden: Steinkopf, 1911), p. 35 ff.; in Alexander, *Colloid Chemistry* (New York: Chemical Catalog Co., 1926), Vol. I, chap. 2; Odén, *Arkiv Kemi Mineral. Geol.*, **7**, No. 26 (1920); Andrén, *Diss.*, Upsala, 1918, found similar relations to hold for vapor condensation within a rather wide range of conditions.

of the condensing substance, i.e., the ratio of the amount in solution in excess of the normal solubility to the solubility; thus,  $N = J(P/L)$ . The value of  $J$  appears to be approximately constant, in order of magnitude, for many inorganic substances precipitated from solutions of ordinary viscosity in the absence of added nuclei or foreign materials that would retard crystallization. Different colloids may therefore be prepared having similar dispersities simply by choosing the conditions of condensation to give equal values of  $P/L$ . To obtain submicroscopic particles in such cases,  $P/L$  must equal or exceed  $10^4$  to  $10^5$ . Since the magnitude of  $P$  is restricted either by solubilities or by the necessity of avoiding high concentrations if the colloid is not to be pasty or solid,  $L$  must be very low (e.g.,  $10^{-6}$  g/cm<sup>3</sup>) in the preparation of highly dispersed colloidal solutions. If the rate of nuclear growth is greatly retarded by the addition of some highly adsorbed substance, a lower rate of nuclear formation and a smaller  $P/L$ , nevertheless, lead to typical colloidal solutions; this is the case when silver chloride or barium sulfate is formed by double decomposition in the presence of gelatin.

If the rate of molecular rearrangement is greater than the rate of deposition, the particles formed are crystalline. X-ray analysis shows that colloidal solutions of metals usually contain crystalline particles having the same structure as the metal in bulk.<sup>12</sup> Dispersions formed by the method of Polanyi and Bogdandy (Table XXIV) are however exceptional; not the least evidence of crystallinity was evident in the case of silver, bismuth, or cadmium.<sup>13</sup> Well-defined salts like the silver halides and barium sulfate normally give crystalline particles when formed from solutions. On the other hand, sulfur, selenium, and the sulfides, oxides, and hydroxides of the metals and metalloids all show very little, if any, crystallinity by X-ray analysis when they are precipitated rapidly from cold concentrated solutions. However, when precipitation is carried out slowly from hot solutions and in the presence of suitable electrolytes, a faint diffraction pattern frequently occurs, which becomes more pronounced upon aging.<sup>14</sup>

When the particles are crystalline, X-ray analysis also reveals their chemical composition. Thus, it has been found that "copper" sols by Bredig's method contain cupric oxide: "ferric hydroxide" may contain  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$  (goethite or lepidocrocite) or  $\text{Fe}_2\text{O}_3$ ; the hydroxides of beryllium and zinc exist in two crystalline forms; there are also two forms of  $\text{Al}(\text{OH})_3$  and two forms of  $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ; and no detectable crystalline hydroxides of tetravalent silicon, tin, lead, titanium, zirconium, and manganese or of the nobler metals precede the formation of the crystalline anhydrous oxides. These results are of special interest in connection with the long-standing debate as to whether the precipitation of

<sup>12</sup> Scherrer, in Zsigmondy, *Kolloidchemie* (3d ed., 1920), p. 387; Björnsthåhl, *Diss.*, Upsala, 1924.

<sup>13</sup> Bogdandy, Böhm, and Polanyi, *Z. Physik*, **40**, 211 (1926).

<sup>14</sup> Böhm, *Kolloid-Z.*, **42**, 276 (1927); a bibliography is given for most of the earlier X-ray analyses of colloids. Currie, *J. Phys. Chem.*, **30**, 236 (1926); Fricke, *Kolloid-Z.*, **49**, 229 (1929); Simon, *ibid.*, **46**, 161 (1928); Blitz, *et al.*, *Z. anorg. Chem.*, **172**, 273, 293 (1928).

these elements from aqueous solutions yields hydroxides or oxides that absorb more or less water.<sup>15</sup> Unfortunately the initial particles are normally practically amorphous, so that X-ray methods are helpless. It is probable however that hydroxides of iron, silicon, tin, etc., are initially formed in spite of the apparent proof by van Bemmelen and others to the contrary and of the absence of crystalline hydroxides. To such highly dispersed and amorphous compounds having very low dissociation pressures, high adsorptive capacities, and great tendencies to polymerization, the ordinary criteria for phase-equilibria and for the existence of stoichiometric compounds can not be applied as readily as was formerly thought to be the case.

(64) **Stability of Colloidal Solutions:** Unless conditions are favorable, a colloidal solution may be a very transient system. An emulsion of a pure hydrocarbon oil in pure water soon flocculates unless the concentration is exceedingly low. Colloidal particles of pure silver in a mixture of toluene and naphthalene<sup>1</sup> readily agglomerate and settle out. Silver iodide precipitated from dilute, exactly equivalent solutions quickly flocculates, but if a slight excess of either reactant is present, a relatively stable sol is obtained. A general consideration of the stability of colloidal solutions reveals two important stabilizing agencies, viz., solvation and electric double-layers, the former being typical of lyophiles, the latter of lyophobic.

*Lyophiles:* Solvation refers to the combination or mutual interaction between solvent and solute in ordinary solutions; the same reaction is operative in lyophilic colloidal solutions (cf. p. 659), particularly in the macromolecular solutions formed spontaneously. Presumably the interaction of the electric fields of adjacent molecules of the colloid and an "active" solvent leads to mutual attractions and orientations<sup>2</sup> that prevent the dispersed particles from colliding so closely as to adhere. In general, solvation occurs as the sole stabilizing agency only in low-conductivity dispersions of macromolecular organic colloids, as rubber, cellulose esters and ethers, polysaccharides, proteins, gums, and the like. Possibly on account of the variety of types of atomic groupings that can occur in a single macromolecule and the corresponding necessity of solvating them with different kinds of solvent molecules, a mixture of liquids is often a better dispersing agent than any single liquid of the mixture, e.g., nitrocellulose in ether-alcohol. The qualities that make a solvent active in this sense are but vaguely understood; at present the only general guide is "like dissolves like."<sup>3</sup>

<sup>15</sup> Weiser, *The Hydrous Oxides* (1926); Symposium on *Oxyhydrates*, *Z. angew. Chem.*, **42**, 595, 885 (1929); Kraut, *Kolloid-Z.*, **49**, 353 (1929); Schwartz and Richter, *Ber.*, **62**, 31 (1929); Dilthey and Hölterhoff, *ibid.*, **62**, 24 (1929); Hüttig and Garside, *Z. anorg. Chem.*, **179**, 49 (1929); Thiessen, *et al.*, *ibid.*, **181**, 417 (1929); **182**, 343 (1929).

<sup>1</sup> Bogdandy, Böhm, and Polanyi, *loc. cit.* A silver sol in pure alcohol is also unstable, according to Giles and Salmon, *J. Chem. Soc.*, **123**, 1597 (1923).

<sup>2</sup> *Die Molekularassoziation*, by Errera in *Dipolmoment und Chemische Struktur*, Leipzig lectures (Leipzig: S. Hirzel, 1929), p. 105.

<sup>3</sup> Highfield, *Trans. Faraday Soc.*, **22**, 57 (1926); McBain, *J. Phys. Chem.*, **30**, 239 (1926); Sheppard, Carver, and Houck, *Fifth Colloid Symposium*, 1927, p. 243; Whitby, McNally, and



Whenever lyophobic particles combine with (or "adsorb") the particles of a solvated colloid without loss of the solvated condition, the aggregate shows the stability of a lyophilic colloid. This "protective action"<sup>4</sup> is often put to practical use in the preparation of dispersions that would otherwise be quite short-lived. The effectiveness of stabilization, as might be expected, is a specific property of both colloids and of the medium, and cannot at present be predicted.

*Lyophobes:* Electric double-layers are responsible for the stability of most hydrosols of inorganic substances, in the absence of protective colloids. The sensitivity of the double-layer to electrolytes (cf. p. 636) is reflected in the sensitivity of the stability of these dispersions to electrolytes.

As two particles carrying electric double-layers approach very close, the outer layers are deformed (or polarized) and an electrical repulsion results. The electrokinetic potential necessary to prevent adhesion upon collision is usually about 15 to 25 millivolts.<sup>5</sup> Since the potential of non-ionogenic and most sparingly-soluble ionogenic particles in pure water is not so large, stability usually requires the presence of a definite amount of an electrolyte one ion of which is adsorbed by the particle. In the preparation of many inorganic colloids by condensation, the stabilizing ion is furnished by a reactant in excess or by a product formed during the process. The following well-known colloids have the charges indicated and are believed to be stabilized by the accompanying electrolyte: Odén S(-), polythionic acids; As<sub>2</sub>S<sub>3</sub>(-), H<sub>2</sub>S; AgI pptd. by excess KI(-), KI; SnO<sub>2</sub>·xH<sub>2</sub>O(-), Na or K stannate; SiO<sub>2</sub>·xH<sub>2</sub>O(-), Na or K silicate; Fe<sub>2</sub>O<sub>3</sub>·xH<sub>2</sub>O(+), normal or basic ferric salts; Pt by Bredig's method (-), platonic acids; Au by reduction (-), aurates or chloraurates.<sup>6</sup>

Excess electrolytes in a colloidal solution may be removed through membranes by dialysis, ultrafiltration, or electrodialysis,<sup>7</sup> or the colloid may be flocculated, washed, and redispersed in a suitable electrolyte solution.<sup>8</sup> Under favorable conditions, these operations can be carried out without changing the particle size.<sup>9</sup>

*Transition Types:* The non-electrocratic, lyophilic and the electrocratic, lyophobic colloids are extreme types between which there are many intermedi-

Gallay, *Sixth Colloid Symposium*, 1928, p. 225; Mardles, *Kolloid-Z.*, 49, 11 (1929); Kraemer and Williamson, *J. Rheology*, 1, 76 (1929).

<sup>4</sup> Zsigmondy, *Kolloidchemie* (5th ed.; 1925), p. 227; Freundlich, *Colloid and Capillary Chemistry* (1926), p. 589; Thomas, in Bogue, *Colloidal Behavior* (1926), Vol. 1, p. 346.

<sup>5</sup> This is the "critical potential" of Powis, *Z. physik. Chem.*, 89, 186 (1915). In exceptional cases, with univalent ions, dispersions are unstable although the electrokinetic potential, as calculated by Equation (57.3) is quite high; see Kruyt, Roodvoets, and van der Willigen, *Fourth Colloid Symposium* (1926), p. 304.

<sup>6</sup> Pauli and Valko, *Electrochemie der Kolloide* (Vienna: Springer, 1929).

<sup>7</sup> Various schemes are described by Holmes, *Laboratory Manual of Colloid Chemistry* (New York: John Wiley and Sons, 1928), and by Hebler, in Liesegang, *Kolloidchemische Technologie* (1927), p. 70.

<sup>8</sup> The reversal of a flocculation is also called "peptization."

<sup>9</sup> Odén, *Nova Acta Upsal.*, 3, No. 4 (1913), for sulfur; in Alexander, *Colloid Chemistry*, Vol. I, chap. 58, for BaSO<sub>4</sub>.

ate cases combining both stabilization agencies in more or less degree. Aqueous colloidal solutions of Odén sulfur, silicic and stannic acids, and some metal hydroxides are electrocratic dispersions with distinct lyophilic properties, and aqueous protein solutions are essentially lyophilic with evident electrocratic behavior. In the case of certain proteins it is possible by control of the solvent composition to produce any one of the different types. These relations may be illustrated in a scheme suggested by Kruyt, depicted in Fig. 40.

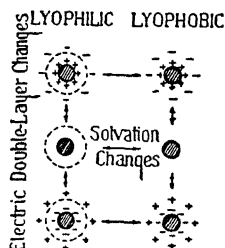


FIG. 40. Variations in Stability Conditions in Sols with Dual Stability, e.g., Egg Albumin. Dotted circle represents solvation sheath, which may be removed from lyophilic (positive, isoelectric, or negative) with desolvating agents (e.g., alcohol), giving corresponding positive, isoelectric, or negative lyophobic sols. Either the lyophilic or the lyophobic sols may be given various electrical states by control of the electrolyte content. Coagulation occurs only in the isoelectric, lyophobic state.

(65) **Changes in State of Colloidal Solutions:** As Graham emphasized, colloidal solutions are metastable systems that are prone to undergo various kinds of changes after no, or apparently very little, change in conditions. For the purpose of discussion, changes in a single particle and changes in the mutual relations of particles may be considered separately even though they often go hand in hand.

*Intra-particle Changes:* The substances making up the colloid particle may be chemically unstable, and they may be in a metastable state of aggregation. A single macromolecule of the intrinsic colloids—proteins, polysaccharides and their derivatives, rubber and other unsaturated polymeric hydrocarbons, synthetic polyacids, polyalcohols, polyesters, polyhydroxy-polybasic acids, and similar substances—contains numerous chemically active groups, which may decompose or react with each other or with the solvent in the many ways familiar to organic chemists. Even the inorganic colloids are subject to spontaneous chemical changes, e.g., the polythionic acids adsorbed on a sulfur particle gradually decompose; the chloride or basic chloride in ferric hydroxide sol may continue to hydrolyze; the initially low-molecular weight silicic acid or stannic acid of fresh sol loses water and polymerizes. With added reagents, colloidal particles react chemically as might be expected, but with greater speed because of the fineness of subdivision.

The principal change in aggregation occurring within colloid particles is the crystallization of amorphous material or the transformation from a metastable

to a stable crystalline form. These changes are most clearly revealed by X-ray analysis (cf. p. 656).

There is reason to believe that some lyophilic sols contain particles possessing the capacity to imbibe solvent and swell (cf. p. 683). Changes in the degree of swelling of such particles may therefore be the cause of the marked differences in viscosity that some colloids, e.g., gelatin, rubber, and nitrocellulose, display under various conditions.<sup>1</sup> Sponge-like particles of this sort are often susceptible to more complete disaggregation by a suitable change in solvent. Lyophobic sols prepared by peptizing a precipitate are also apt to contain aggregates which can be more completely disintegrated by means of a more active peptizing agent.

*Inter-particle Changes:* The most obvious and most studied change in the state of colloidal solutions is the coagulation of the particles following the elimination of the stabilizing factors. Other inter-particle changes are, however, also important. Thus, owing to the increased solubility of very small particles, the larger particles in a dispersion grow at the expense of the smaller until eventually the dispersed material is no longer colloidal, but grossly crystalline. The rapidity of the recrystallization depends upon the solubility; in a Carey Lea silver sol, obvious crystals developed in the course of four years, and, in a manganese arsenate dispersion, less than a year was sufficient.

In many cases a relatively slight aggregation occurs without continuing through the stages of complete coagulation; that is, an aggregate of primary particles may possess a normal degree of stability. The red-to-blue color change in Faraday gold sols upon the addition of insufficient electrolyte to precipitate them is due to such a partial aggregation. Varying degrees of partial aggregation are also likely to occur in the high-viscosity lyophilic dispersions.<sup>2</sup> Rather direct evidence of such a condition is provided by the rigidity and elasticity, on a microscopic scale, of apparently fluid sols of gelatin or soap.<sup>3</sup>

*Coagulation:* Many agencies are capable of causing the coagulation (or flocculation) of colloidal solutions: decrease in temperature (without freezing the medium), as for hydrosols of gelatin, agar, and Odén sulfur; freezing the medium, as for lyophobic sols; increase in temperature, as for alcossols of nitrocellulose,<sup>4</sup> cellulose sols in sodium hydroxide solution,<sup>5</sup> and organo- or hydro-sols of metals; light, as for gold<sup>7</sup> and silver hydrosols; X- and  $\beta$ -radiation, as for

<sup>1</sup> Loeb, *Proteins and the Theory of Colloidal Behavior* (2d ed.; 1924), pp. 259, 280, 299. Cf. the discussion of non-Newtonian flow in colloidal solutions, p. 564.

<sup>2</sup> See references of footnote 1, p. 548.

<sup>3</sup> Freundlich and Seifriz, *Z. physik. Chem.*, **104**, 233 (1923), observed the motions of a microscopic nickel particle displaced magnetically in the sols.

<sup>4</sup> Kugelmass, *Rec. trav. chim.*, **41**, 751 (1922).

<sup>5</sup> Beltzer, *Kunststoffe*, 203 (1912)

<sup>6</sup> Lindemann and Svedberg, *Kolloid-Z.*, **29**, 1 (1921); Burton and Deacon, *Sixth Colloid Symposium* (1928), p. 77.

<sup>7</sup> Nordenson, *Diss.*, Upsala (1914).

<sup>8</sup> Kraemer, *Second Colloid Symposium* (1924), p. 57.

ceric oxide and Bredig's copper hydrosols; <sup>9</sup> mechanical stirring, as for ferric oxide sol; <sup>10</sup> electric field, as in water-in-oil emulsions; <sup>11</sup> "tanning" agents, as formaldehyde or tannic acid on gelatin; addition of non-solvent liquid, as water to an acetone solution of nitrocellulose; "salting-out" by high concentrations of electrolytes, as of egg albumin by saturated ammonium sulfate; dilute electrolytes, as for most hydrophobic sols; chemical destruction or removal, as by dialysis, electrodialysis, etc., of a stabilizing agent; mutual coagulation of two hydrophobic sols; or mutual coagulation of a lyophobic and a lyophilic sol.

The exact nature of the changes leading to the loss of the stabilizing factors is in many cases not easily identified. Not infrequently the colloidal particle or its surface is chemically changed with the formation of substances the colloidal state of which is unstable under the resulting conditions. The coagulation of gelatin by formaldehyde or tannic acid provides an example for a lyophilic colloid, and the oxidation of a hydrosol of cadmium, lead, or other reactive metal provides a similar example for the lyophobic class.

Disregarding cases involving definitely chemical changes, one may state that the coagulation of lyophilic systems generally follows the addition of "non-solvents" to the dispersion medium (cf. Fig. 39). The amount of non-solvent necessary to cause a specified degree of coagulation in a given quantity of dispersion is often used as a measure of the "solubility" or "solvation" of such lyphiles as rubber, cellulose derivatives, and other macromolecular substances.<sup>12</sup> It is obvious that this is in no way related to solubility in the strict phase-rule sense. True solubility usually cannot be defined for a macromolecular solute, for the typical lyophilic dispersions are rarely homogeneous (cf. p. 543). As a consequence, the composition and properties of the coagulated material vary at different stages of the precipitation, and the apparent solubility in liquids of limited dispersing power is dependent on the quantity of solid phase present.<sup>13</sup> The relation between the chemical natures of the components of a lyophilic system and the coagulating values of non-solvents, whether electrolytes or non-electrolytes, is as impossible of quantitative theoretical explanation as are solubilities in ordinary solutions.

(66) **Electrolyte Coagulation of Hydrophobic Colloids:** <sup>1</sup> In spite of the great theoretical and practical importance of lyophilic systems, the bulk of coagulation studies have dealt with lyophobic and particularly with hydrophobic

<sup>9</sup> Fernau and Pauli, *Kolloid-Z.*, **20**, 20 (1917); Crowther, *Phil. Mag.*, **7**, 86 (1929).

<sup>10</sup> Freundlich and Loebmann, *Kolloidchem. Beih.*, **28**, 391 (1929).

<sup>11</sup> Clayton, *Theory of Emulsions and Their Technical Application* (4th ed.; 1943).

<sup>12</sup> Mardles, *Kolloid-Z.*, **49**, 4 (1929); Whitby and Gallay, *Trans. Roy. Soc. Can.*, **23**, 1 (1929).

<sup>13</sup> Sørensen (globulins), *J. Am. Chem. Soc.*, **47**, 457 (1925); Pummerer (rubber), *Kautschuk*, **5**, 129 (1929); Kumichel (nitrocellulose), *Kolloidchem. Beih.*, **26**, 161 (1928); W. Ostwald, *et al.*, *Kolloid-Z.*, **49**, 314 (1929) and earlier papers, dealing with "Bodenkörper" effects in general.

<sup>1</sup> A detailed discussion and review of this topic (up to 1929) is given by Pauli and Valkó, *Elektrochemie der Kolloide*. The summaries of Bancroft, *Applied Colloid Chemistry*, chap. 10, and of Freundlich, *Colloid and Capillary Chemistry*, p. 415 ff., are also important. The whole subject has been revolutionized in Verwey and Overbeek, *Theory of the Stability of Lyophilic Colloids* (New York: Elsevier Publishing Co., 1948).

colloids. Schulze<sup>2</sup> and others early recognized the greater coagulating efficiency of electrolytes with polyvalent ions, and Hardy<sup>3</sup> discovered the parallelism between the effects of electrolytes on electrophoresis and on the stability and coagulation of hydrophobic colloids. The Schulze-Hardy-Powis rule states that hydrophobic colloids coagulate when the electrokinetic potential is reduced below a critical value<sup>4</sup> by adsorption of an ion of opposite sign, the effectiveness of the ion increasing rapidly with its valence.

TABLE XXV  
COAGULATION VALUES FOR TYPICAL HYDROSOLS IN MILLIMOLES OF  
COAGULATING ION PER LITER

Negative arsenic trisulfide sol <sup>1</sup>		Positive ferric oxide sol <sup>2</sup>	
Salt	Coag. value	Salt	Coag. value
AlCl <sub>3</sub> .....	0.062	K <sub>4</sub> Fe(CN) <sub>6</sub> .....	0.067
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> .....	0.074	K <sub>3</sub> Fe(CN) <sub>6</sub> .....	0.096
FeCl <sub>3</sub> .....	0.14	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> .....	0.19
Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> .....	0.22	K <sub>2</sub> tartrate.....	0.20
PbCl <sub>2</sub> .....	0.23	K <sub>2</sub> SO <sub>4</sub> .....	0.22
HgCl <sub>2</sub> .....	0.32	K <sub>2</sub> oxalate.....	0.24
28 inorganic M <sup>++</sup> -salts.....	0.9-2.1	K <sub>2</sub> CrO <sub>4</sub> .....	0.33
KNO <sub>3</sub> .....	105.	KIO <sub>3</sub> .....	0.90
* * * * *	* * * *	KBrO <sub>3</sub> .....	31.
7 inorganic M <sup>++</sup> -salts.....	0.6-0.8	KCNS.....	47.
KNO <sub>3</sub> , KCl.....	50.	KCl.....	103.
K formate.....	86.	KClO <sub>3</sub> .....	116.
K acetate.....	110.	KNO <sub>2</sub> .....	131.
K <sub>2</sub> SO <sub>4</sub> .....	66.	KBr.....	138.
K <sub>3</sub> citrate.....	>240.	KI.....	154.
Aniline HCl.....	2.5	K formate.....	173.
Morphine HCl.....	0.4		

<sup>1</sup> Above asterisks: Linder and Picton, *J. Chem. Soc.*, 67, 63 (1895). Below asterisks: Freundlich, *op. cit.*, p. 420.

<sup>2</sup> Weiser and Middleton, *J. Phys. Chem.*, 24, 30 (1920).

Quantitative comparisons are usually made in terms of the "coagulation value," i.e., the minimum concentration necessary to bring about coagulation under specified conditions. Since there is no single concentration sharply separating stability and coagulation, the coagulation value is rather arbitrary and depends not only upon the colloidal solution and the coagulating agent, but

<sup>2</sup> *J. prakt. Chem.*, 25, 431 (1882); 27, 320 (1883); see also Linder and Picton, *J. Chem. Soc.*, 67, 63 (1895); 87, 1906 (1905).

<sup>3</sup> *Proc. Roy. Soc., A*, 66, 110 (1900).

<sup>4</sup> It was originally thought that the isoelectric condition is necessary for coagulation.

also upon the conditions under which coagulation is carried out and upon the manner in which the coagulated state is defined and observed. The coagulation value is also ambiguous in that it does not distinguish between the total concentration of coagulating electrolyte and the amount that enters the double-layer and is directly responsible for the loss of stability. Unfortunately, a more accurate estimate of coagulating power is usually quite difficult to make.

Table XXV, summarizing some coagulation values typical of heteropolar colloidal particles, illustrates the following features: the dominant effect of the valence of the oppositely-charged ion among the inorganic ions, and the relatively small effect of the ion having the same sign as the particle; the tendency for the ion with the same sign to exert an antagonistic, stabilizing action; the

TABLE XXVI  
COAGULATION VALUES AND ELECTROKINETIC POTENTIALS FOR A NEGATIVE  
COLLOIDION HYDROSOL WITH A pH 5.8

Coagulating electrolyte	Coagulation value millimoles per liter of cations	Crit. potential millivolts
LiCl.....	500-250	10-16 $\pm$ 2
NaCl.....	500-250	10-14 $\pm$ 2
KCl.....	250-125	14-21 $\pm$ 2
Na <sub>2</sub> SO <sub>4</sub> .....	500-250	13-19 $\pm$ 2
Na <sub>4</sub> Fe(CN) <sub>6</sub> .....	500-250	13-21 $\pm$ 2
MgCl <sub>2</sub> .....	60-30	11-15 $\pm$ 2
MgSO <sub>4</sub> .....	60-30	15-19 $\pm$ 2
CaCl <sub>2</sub> .....	30-15	14-17 $\pm$ 2
LaCl <sub>3</sub> .....	0.50-0.25	14-21 $\pm$ 2

appreciable variation in the values for ions of the same valence and chemical character, particularly among the univalent ones; the greater effectiveness of heavy-metal and organic ions, compared to light-metal and inorganic ions of the same valence; and the transition cases that prevent a sharp distinction between various valence types. Additional data could be given to show that hydrogen and hydroxyl ions, either as coagulating ion or as stabilizing ion, usually are more effective than other ions of their valence-class.

Table XXVI displays similar features for the coagulation of nonpolar colloidal particles <sup>5</sup> and, in addition, illustrates the close relation between coagulation and electrokinetic behavior. The larger concentration and the smaller potential specify the conditions for coagulation in less than 12 hours; the smaller concentration and the larger potential represent the maximum concentration and minimum potential at which there was no detectable coagulation. The critical potential was approximately 16 mv, regardless of the coagulating electrolyte; the same was true for coagulations at pH 3 and pH 11. The parallelism between coagulation and zeta potential has also been demonstrated by

<sup>5</sup> Loeb, *op. cit.*, p. 90.

Tuorila <sup>6</sup> in a very detailed way by comparisons of the rates of coagulation at various potentials.

The parallelism between coagulation and zeta potential is also demonstrated by "charge reversal;" e.g., ferric chloride may be added to a negative platinum sol <sup>7</sup> in excess of the coagulating amount, giving a positive platinum sol stabilized by adsorption of ferric ions. The positive sol may be coagulated by much higher concentrations of ferric chloride, corresponding to the usual low coagulating power of chloride ion. A number of similar cases are known.<sup>8</sup>

The data of Table XXVII <sup>1</sup> can be interpreted as illustrating a pure valence effect if the assumptions are made that these 23 cations, on account of their chemical similarity, are all adsorbed in accordance with a single parabolic

TABLE XXVII <sup>1</sup>  
COAGULATION OF  $As_2S_3$  SOL BY COMPLEX COBALT-AMMINE SALTS

Number of salts	Valence	Coagulation values micromoles per liter		
		Range	Mean	Calcd.
7	1	4670-6670	5430	5430
5	2	333-400	360	340
6	3	53-80	67	67
4	4	17-21	19	21
1	6	—	4.2	4.2

<sup>1</sup> Matsuno, *J. Coll. Sci. Imp. Univ. Tokyo*, **41**, No. 11 (1921); see also, Freundlich and Zeh, *Z. physik. Chem.*, **114**, 65 (1925).

equation; that the effect of the anion is negligible; and that the same reduction in charge on the particle is necessary to reach the critical potential. If these are true, electro-equivalents of the different cations must be adsorbed, and if the amounts adsorbed are negligible compared to the coagulation values, the latter should be related in accordance with the equation:  $a/\text{valence} = k(\text{coag. value})^n$ , where  $k$  and  $n$  are the constants of the adsorption isotherm, and  $a$  is the amount of univalent cation adsorbed for coagulation. Best values of  $k/a$  and  $n$  ( $= 0.25$ ) were determined empirically and the corresponding coagulation values of the last column were calculated. Independently of hypotheses, coagulating power, i.e., the reciprocal of the coagulation value, is in this particular case proportional to the fourth power of the valence. However, this fact offers no evidence for the validity of the assumptions, none of which was

<sup>6</sup> *Kolloidchem. Beih.*, **27**, 44 (1928).

<sup>7</sup> Quantitative data are given by Buxton and Teague, *Z. physik. Chem.*, **57**, 64 (1907); see also Freundlich, *op. cit.*, p. 428.

<sup>8</sup> If the first coagulation region were overlooked (as actually happened), the ferric chloride would appear to have an unusually high coagulation value, in view of its valence, and would appear to fall with univalent cations, giving a so-called *irregular ionic series*. Although charge reversals are now understood, the initial unsuitable name is still sometimes used.

tested. It is unlikely that the amount of the hexavalent ion adsorbed is negligible, and there is no particular reason to suppose that such complex ions are equally adsorbed.<sup>9</sup>

*Mutual Coagulation:* The stabilizing electrolyte of one sol may react with that of another sol with the simultaneous reduction of the potential on both kinds of particles and mutual coagulation.<sup>10</sup> Since reactions between electrolytes are usually metathetical, mutual coagulation is much more often observed between colloids of opposite sign, but may also occur when the signs are the same.<sup>11</sup> When a large excess of either colloid is used, the proportions being compared in terms of the stabilizing agents, coagulation does not take place, and the composite particles formed have the same sign as the colloid in excess.

In concentrations insufficient to confer a protective action, hydrophilic sols that are capable of reacting with the stabilizing electrolyte of a hydrophobic sol may lead to mutual coagulation or may cause only a *sensitization* of the hydrophobe. This phenomenon has been studied particularly in the case of proteins.<sup>12</sup>

*Kinetics of Coagulation:* Since coagulation is a dynamic process involving the union of colloidal particles, a satisfactory understanding of the process requires the consideration of its rate. Unfortunately in many cases, e.g., lyophilic dispersions in general and some highly dispersed lyophobic systems, the separate particles cannot be perceived, even in the ultramicroscope. As a consequence the kinetics of coagulation in such cases can be investigated only indirectly by following the change in some physical property, such as viscosity, light absorption, or electrical conductivity. Although the change in a physical property may be interesting in itself, it generally cannot yield quantitative information concerning the kinetics of the combination of particles, which is the basic process in coagulation. The development of this aspect of coagulation has therefore had to depend largely upon investigations of lyophobic systems containing ultramicroscopically visible particles.

Upon observing that the time required for the red-to-blue color change in gold sols (presumably representing a definite degree of coagulation) reaches a constant minimum value above a fairly sharply defined electrolyte concentration and is independent of the kind of electrolyte, Zsigmondy<sup>13</sup> concluded that the rate of coagulation under such conditions must be dependent only on the rate of collision of the particles, i.e., on their concentration and their Brownian motion. Such coagulation is "rapid" in contradistinction to "slow coagulation," in which the rate depends upon the concentration and kind of coagulating electrolyte. Rapid coagulation, in this sense, sets in when the zeta potential is practically zero.

<sup>9</sup> Similar data for a ferric oxide sol by Freundlich and Zeh, *loc. cit.*, were not so simply related as those of Matsuno.

<sup>10</sup> A general summary is given by Thomas, in Bogue, *Colloidal Behavior*, Vol. I, chap. 13.

<sup>11</sup> Freundlich and Nathansohn, *Kolloid-Z.*, 28, 258 (1920); 29, 16 (1921).

<sup>12</sup> Freundlich, in Bogue, *Colloidal Behavior*, Vol. I, chap. 12.

<sup>13</sup> *Z. physik. Chem.*, 92, 600 (1917).



Smoluchowski<sup>14</sup> developed the quantitative relations for rapid coagulation in a dispersion of spheres of uniform size on the assumption that two particles adhere whenever Brownian motion causes them to approach within a certain distance  $R$ . This situation may be compared to the collision theory of bimolecular reactions with its "frequency factor." Making approximate corrections for the differences in the Brownian motion and in  $R$  for double-, triple-, etc., particle aggregates, he obtained, as a final result, the equations

$$n_k = \frac{n_0(t/T)^{k-1}}{(1 + t/T)^{k+1}} \quad \text{and} \quad n = \frac{n_0}{1 + t/T} \quad (66.1)$$

where  $n_k$  is the number of aggregates of the  $k$ -order at the time  $t$ ,  $k$  is the number of primary particles in the aggregate,  $n_0$  is the initial number of particles, and  $T$

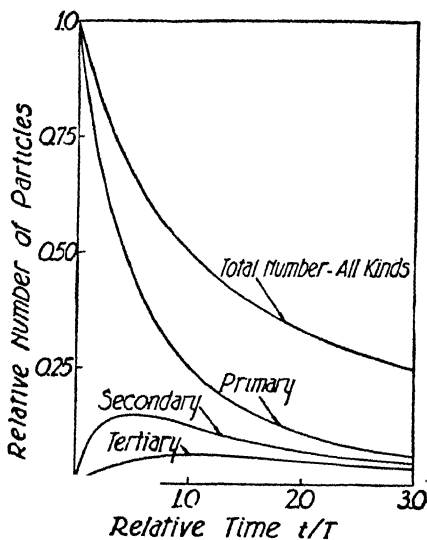


Fig. 41. Kinetics of Coagulation According to von Smoluchowski's Theory.

is a constant characterizing the rate of coagulation and theoretically equal to  $1/(4\pi n_0 DR)$ ,  $D$  being the diffusion constant. In practice,  $T$  is an empirical constant giving the time for the total number of particles to fall to one-half.<sup>15</sup> The results are represented graphically in Fig. 41.

For slow coagulation, Smoluchowski suggested that only a fractional number  $\epsilon$  of the collisions between particles leads to permanent unions.<sup>16</sup> This does not require any modification of Equation (66.1), but it increases  $T$  in proportion; i.e.,  $T = 1/(4\pi n_0 DR\epsilon)$ .

Smoluchowski's theory for rapid coagulation has been reasonably well confirmed, considering the experimental difficulties, by a number of investigators using direct counting methods.<sup>17</sup> Discrepancies frequently appear toward the end of coagulation. Indeed, on account of the approximations involved, the equations cannot be

<sup>14</sup> *Physik. Z.*, **17**, 585 (1916); *Z. physik. Chem.*, **92**, 129 (1917).

<sup>15</sup> It may incidentally be noted that coagulation, with respect to the rate of change of all particles, is equivalent to an ideal polymerization reaction of the second order; the specific rate  $k$  is equal to  $1/(Tn_0)$ .

<sup>16</sup> See also Freundlich's theory of slow coagulation, *Kolloid-Z.*, **23**, 163 (1918).

<sup>17</sup> Zsigmondy, *loc. cit.*; Westgren and Reitstötter, *Z. physik. Chem.*, **92**, 750 (1917); *J. Phys. Chem.*, **26**, 537 (1922); Kruyt and van Arkel, *Rec. trav. chim.*, **39**, 656 (1920); Lachs and Goldberg, *Kolloid-Z.*, **31**, 116 (1922); Ehringhaus and Wintgen, *Z. physik. Chem.*, **104**, 301 (1923); Tuorila, *Kolloidchem. Beih.*, **22**, 191 (1926); **24**, 1 (1927); **27**, 44 (1928).

expected to be applicable except during the early stages. The ratio of  $\bar{R}$  to the particle radius, which can be calculated from  $T$ , falls between 2 and 3 under favorable conditions (well-defined sols with uniform particles, painstaking technic, etc.). Upon the assumption that any variation from the value 2 is due to experimental errors, this means that two particles must actually touch in order to adhere.

The experimental results for slow coagulations are not so consistent.<sup>18</sup> Although the theory may be somewhat oversimplified to deal adequately with slow coagulation, it is also possible that discrepancies are in part due to the greater sensitivity of slow coagulation to variations in particle size and to deviations from spherical shape.

Müller<sup>19</sup> has calculated the effects of these two factors on the coagulation rate. Qualitatively expressed, non-uniformity in size or non-sphericity leads to a considerable increase in the rate of coagulation; the rate of coagulation of rod-particles departs much more than that of plate-particles from the original Smoluchowski theory. The differences are more marked in slow coagulations than in rapid coagulations. The extended theory has been fairly well confirmed by direct counting methods.<sup>20</sup>

*Reversal of Coagulation:* The coagulum of lyophilic sols often can be redispersed by simple reversal of the conditions that caused coagulation; for instance, gelatin and soap gels are reconverted to sols by warming, and a nitrocellulose precipitated by water from acetone may be redispersed in pure acetone. Occasionally over-shooting an exact reversal is necessary; for instance, agar gel must be heated to ca. 90° for redispersion, although gel formation requires cooling to ca. 40°. Whenever coagulation of a lyophile cannot be reversed, a suspicion is justified that chemical changes accompanied the coagulation, or that the irreversibility is apparent, being due to a low rate of redispersion. The irreversible coagulation of viscose and egg albumin by heat and of gelatin by formaldehyde undoubtedly involves chemical changes; decomposition of the cellulose xanthate, "denaturation" of the albumin, and formation of addition compounds in the case of gelatin.

The reversal of coagulation in lyophobic systems is more restricted. Unprotected metal hydrosols are rarely reversible. The electrolyte coagulation of inorganic hydrous oxides, halides, ferrocyanides, sulfides, sulfur, selenium, clay, and similar substances can frequently be reversed by immediately washing out the coagulating agent and treating the coagulum with a solution of a stabilizing electrolyte. Ease of peptization decreases greatly if the coagulum is allowed to age or to dry out. Reversibility is commonly secured in commercial colloids, e.g., pharmaceutical preparations, which would otherwise be irreversible, by the addition of lyophilic protective colloids.

<sup>18</sup> Fair agreement was found by Westgren, *Arkiv Kemi Mineral. Geol.*, **7**, No. 6 (1918); Tuorila, *loc. cit.*; Wiegner and Marshall, *Z. physik. Chem.*, **140**, 39 (1929). In other cases, the theory was not confirmed, Krut and van Arkel, *Rec. trav. chim.*, **40**, 169 (1921); *Kolloid-Z.*, **32**, 29 (1923); Tuorila, *loc. cit.*

<sup>19</sup> Müller, *Kolloid-Z.*, **38**, 1 (1926); *Kolloidchem. Beih.*, **26**, 257; **27**, 223 (1928).

<sup>20</sup> Tuorila, *loc. cit.*; Wiegner and Marshall, *loc. cit.*

Odén has found that freshly coagulated Carey Lea silver, barium sulfate, and Odén sulfur can be reprecipitated without any appreciable change in particle size. The last case is particularly striking in that the reversibility is so complete for coagulation by either cooling or electrolytes. Furthermore, the temperature and electrolyte concentration for peptization show a well-defined variation with particle size.

(67) **Soaps:** Another class of compounds, the *detergents*, forms stable colloidal solutions in suitable solvents and under otherwise proper conditions. There are three main classes, anion-active, cation-active and nonelectrolytic. Soaps are the best known examples of the first class, with the negative radical being responsible for the surface activity and other colloidal behavior. The sulfonated and sulfated soaps also belong to this group.

It was early recognized that aqueous soap solutions show anomalous colligative properties as well as conductance behavior. On the other hand, the same properties when observed in alcohol solutions are quite normal from the point of view of the theories of electrolytic dissociation. In water solution the properties which depend upon the number of particles present are abnormally low, yet soap solutions have an equivalent conductance which is both higher than can be explained in the usual electrolyte, and quite irregular in concentration dependence.

McBain<sup>1</sup> has explained these phenomena by assuming that the long chain anions aggregate to form ionic micelles, with the size and shape of the micelle being dependent on the concentrations and nature of the detergent. A lamellar arrangement of the soap molecules in the micelle is favored. Since the ions cannot lose their charge, this ionic micelle must be also charged. But owing to the reduced frictional resistance of the micelle compared to the number of ions of which it is composed, in accordance with Stokes's law, the equivalent conductance will be greater than that of the free ions. Thus, McBain and Salmón<sup>2</sup> calculated that if several ions, for example, twelve, associate, the electrical driving force on the aggregate would be twelve fold, whereas the radius of the sphere would be increased by only 2.3 times its original value. The calculated velocity of 5.2 times its initial value is not realized, due as was assumed to the hydration of the charged particle.

Actually, such arguments are too simple, and it was not until closer study was made of the course of the conductance-concentration curves that more precise information was obtained. Even so, there is no single theory for the adequate explanation of the characteristic forms of such curves. In general, they may be divided into three successive regions.

1. A region in which is found an initial slope of equivalent conductance,  $\Lambda$ , versus square root of concentration curve characteristic of strong electrolytes.
2. A critical concentration region in which  $\Lambda$  drops off sharply, and in which the transference number of the surface active ion rises abruptly.

<sup>1</sup> McBain, in Alexander, *Colloid Chemistry*, Vol. I, p. 137; Vol. V, p. 102.

<sup>2</sup> *J. Am. Chem. Soc.*, **42**, 426 (1920).

3. A region in which  $\Lambda$  and transference number remain sensibly constant. Often there is observed a rise in  $\Lambda$  in this range, and it becomes the more pronounced the higher the molecular weight of the paraffin-chain salt.

In order to explain the sharp break in  $\Lambda$ , McBain and others have postulated micelle formation. It is assumed that two types of colloidal particle are formed, one a large neutral micelle which does not contribute to the conductance, and the other the highly charged ionic micelle which has been mentioned. The two types are in equilibrium, the relative amounts of each being dependent upon the concentration of the solution and the temperature. As the solution becomes more concentrated the ionic micelle is formed in greater and greater proportion.

This qualitative description of the behavior of solutions of a colloidal electrolyte such as soap has been criticized by Hartley<sup>3</sup> on the basis that it disregards the effect of the various coulomb forces which exist between the ions and the micelles. This investigator believes that the observed properties of solutions of these electrolytes can be best explained in terms of but one type of micelle. This consists of an ionic micelle formed by the association of a number of high molecular weight ions, to which particle are attached the customary "gegen-ions." According to Hartley the micelle assumes spherical form.

In recent years the alkyl sulfates and sulfonates and their alkali salts have been studied in considerable detail, since with them hydrolysis problems presented in the case of the soaps are largely avoided. Such investigations go back to Reyhler<sup>4</sup> and to Lottermoser,<sup>5</sup> and they have been extensively studied since by Hartley, McBain, Tartar and others. The voluminous literature has been surveyed in several places.

By and large it may be argued that too much attention is being given to discussion of the shape of the micelles when so little information is available concerning the actual size, i.e., the number of primary units of which they are formed. If it were known exactly how many building blocks were required it might be possible at least to eliminate certain proposed over-all forms of the micelles which have been described. In protein chemistry size came before shape, and we believe properly so. And it would appear that just those observations on sedimentation velocity and diffusion constant which have been so successful in the study of the proteins might be useful in this instance. It is true that some early sedimentation velocity experiments with the usual soap solutions<sup>6</sup> have given inconclusive results, apparently due to the fact that the partial specific volumes of these soaps in solution are quite close to unity. But in spite of difficulties it will be seen that a start has been made in the accumulation of size of micelle data.

Lamm and Högberg<sup>7</sup> made a detailed study of diffusion in soap systems, but owing to various complications such as low solubility and hydrolysis their

<sup>3</sup> Hartley, *Aqueous Solutions of Paraffin Chain Salts* (Paris: Hermann et Cie, 1936).

<sup>4</sup> Reyhler, *Bull. Soc. Chim. Belg.*, 27, 110 (1913); *Kolloid-Z.*, 12, 277; 13, 252 (1913).

<sup>5</sup> Lottermoser and Püschell, *Kolloid-Z.*, 63, 175 (1933).

<sup>6</sup> McBain and McBain, *Proc. Roy. Soc.*, A139, 26 (1933).

<sup>7</sup> *Kolloid-Z.*, 61, 10 (1940).

results are not easy to interpret. Miller and Andersson<sup>8</sup> carried out sedimentation and diffusion analyses of alkyl sulfate esters with mixed chains of C<sub>8</sub> to C<sub>18</sub> (Duponol) and found a molecular weight of 12,500 which corresponds to an aggregation number of about 75 molecules of detergent. For a purified sodium lauryl sulfate Hakala<sup>9</sup> found a somewhat higher "molecular" weight for the micelles, namely 22,000. If ellipsoidal shape is assumed for unhydrated micelles the ratio of the lengths of major to minor axes is computed to be five. This is of course a maximum value. Vetter<sup>10</sup> chose for his study the sodium salt of sulfonated di-succinate (Aerosol MA) and carried out extensive diffusion and viscosity experiments to find 23.6 for the aggregation number.

In another new approach Debye and his associates<sup>11</sup> have measured the scattering of light by soap solutions to determine the micellar weight. Dodecyl amine hydrochloride was found to be a suitable solute, and the excess turbidity of the solutions over that of the solvent is negligible until the critical concentration (as determined by electrical conductance) is reached. From this point the change of turbidity with concentration is quite normal and the molecular weight of the micelle is calculated to be 12,300,<sup>12</sup> corresponding to an aggregate of 66 dodecyl amine hydrochloride molecules.

The data are described in terms of the double-layer picture of Mattoon, Stearns and Harkins.<sup>13</sup> It is assumed that the micelle structure represents an equilibrium between the repulsive long-range coulomb forces due to the charges concentrated in the "heads" of the soap molecules and the short range attractive van der Waals forces which come into play when the "tails" are brought from the surrounding water into the hydrocarbon part of the micelle structure.

A more classical mode of attack on the problem of the structure of the micelles is that of X-ray analysis. Unfortunately here the concentration of the solutions must be greater than that which must be used for significant sedimentation velocity, diffusion or viscosity experiments, but valuable information may be gained. Hess and Gunderman<sup>14</sup> demonstrated the presence of platelets which orient during flow.

The property of the micelles to take up within them solutes that would not otherwise be dissolved in water is called solubilization. Studies of Stauff,<sup>15</sup> Kiessig and Philippoff,<sup>16</sup> and Hess<sup>17</sup> suggest that solubilization occurs between the layers of paraffin-chain salt molecules which are assumed to form lamellar micelles, since the spacing between them increased in proportion to the amount of material dissolved. The dissolved oils or other water-insoluble materials

<sup>8</sup> *J. Biol. Chem.*, **144**, 475 (1942).

<sup>9</sup> *Diss.*, University of Wisconsin (1943).

<sup>10</sup> *J. Phys. & Colloid Chem.*, **51**, 262 (1947).

<sup>11</sup> *J. Phys. & Colloid Chem.*, **51**, 18 (1947).

<sup>12</sup> Debye, *J. Phys. & Colloid Chem.*, **53**, 1 (1949).

<sup>13</sup> *J. Chem. Phys.*, **15**, 209 (1947).

<sup>14</sup> *Ber.*, **70**, 1800 (1937).

<sup>15</sup> *Kolloid-Z.*, **89**, 224 (1939).

<sup>16</sup> *Naturwissen*, **27**, 593 (1939).

<sup>17</sup> *Kolloid-Z.*, **88**, 40 (1939).

dilute the hydrocarbon chains in the interior of the micelle. In the beginning the solubility of the oil remains constant as soap is added to the water. But when the critical concentration is reached the addition of more soap causes the solubility to increase rapidly, and it is believed<sup>18</sup> the rate at which the solubility increases also increases as the soap concentration increases. Such solubilization systems are thermodynamically stable.<sup>19</sup>

With the development of the synthetic rubber-like materials a study of the mechanism of emulsion polymerization has become important. A new general theory has been presented by Harkins.<sup>20</sup> In it two types of loci are described, one in which minute polymer particles are initiated, and the other in which most of the polymer is formed. Early in the reaction nearly all of the polymer particle nuclei are formed in monomers stabilized in the core of oil in the soap micelles. Then the polymeric units grow from the soap micelles and extend into the aqueous phase with adsorbed soap. The polymer particles themselves provide the site of preponderant polymer formation. They take up monomer molecules from the aqueous phase and the monomer in the polymer-monomer particles thus formed react to allow more monomer to be taken up. Thus, the function of the monomer emulsion droplets is to serve as a storehouse from which monomer molecules diffuse into the aqueous phase where they are collected by soap micelles and polymer particles for the polymerization reaction.

#### GELS<sup>21</sup>

The physical forms of a coagulated colloid can vary widely depending upon the substance and the manner in which coagulation was brought about. The coagulum may be some sort of precipitate—sandy, granular, curdy, flaky, slimy, or gelatinous—as is usually the case from dilute inorganic sols, or it may be a coherent, more or less elastic solid enclosing a part or all of the dispersion medium. Graham applied the term “gel” to all types of coagula, but it is now commonly restricted to the last form mentioned or to the product of its desiccation. Gels in this restricted sense represent the only form of coagula that has received extensive investigation from the colloid point of view.

When a gel is an apparently homogeneous, transparent, amorphous body with a high liquid content, it is often more specifically referred to as a “jelly” after its prototype, ordinary table jelly. On account of the astonishing rigidity that some jellies containing over 99 per cent of the liquid component may have, the very dilute jellies are frequently represented as typical of the gel state.

<sup>18</sup> Harkins, *J. Am. Chem. Soc.*, **69**, 1428 (1947).

<sup>19</sup> McBain, *Adv. in Colloid Sci.* (New York: Interscience Publishers, 1942), Vol. I; Harkins, Mattoon, and Corrin, *J. Am. Chem. Soc.*, **68**, 220 (1946).

<sup>20</sup> *J. Am. Chem. Soc.*, **69**, 1428 (1947).

<sup>21</sup> For summaries, see Freundlich, *Colloid and Capillary Chemistry* (1926), pp. 658-768; chap. 47-51 in Alexander, *Colloid Chemistry*, Vol. I, by Bradford, Lloyd, Liesegang, and Holmes; Bary, *Les Colloïdes* (Paris: Dunod, 1921); Ostwald, *Kolloid-Z.*, **46**, 248 (1928); von Weimarn, *Jellies and Gelatinous Precipitates* (Tokyo: Koseikai Publishing Dept., 1928); Weiser, *The Hydrous Oxides* (1935); *The Colloidal Salts* (1938); Ferry, *Adv. in Protein Chem.*, IV (New York: Academic Press, 1948).

Whether typical or not, these particular gels present the problems of gel formation and gel structure in most striking form.

Gels with a low liquid content, desiccated gels, or bodies behaving like them are also called "xerogels." This class includes a great many naturally-occurring and synthetic materials, many of them being of great technical importance: opal, limonite, natural and artificial zeolites, silica gel and other inorganic adsorbent gels, soap, leather and leather substitutes, natural and artificial textile fibers, wood, paper, plastics, paint and analogous films, rubber, starch, bread and other foodstuffs, muscle connective tissue, cell membranes, and other organic structures.

As examples of gels that have been the subject of scientific study, the following may be mentioned: gelatin, agar, pectin (fruit), soaps, mercuriosulfosalicylic acid and salts, dibenzoyl cystine, lithium urate, starch—all obtained by cooling suitable hydrosols or solutions; viscose, the "hydrous oxides" of silicon and the metals, especially tin, iron, aluminum, chromium, cerium, the arsenates and phosphates of iron and other metals—all by the electrolyte-coagulation of hydrosols; metastyrene and other polymeric substances by polymerization in solution; cellulose acetate in benzyl alcohol; nitrocellulose in alcohol, nitroglycerin, and other organic liquids.

Gel formation has been considered to be the result of a partial or incomplete precipitation of a sol. This is obviously the case for gels that are formed by suitable control of conditions from sols that otherwise yield precipitates. Silicic and stannic acids, ferric, aluminum and chromium hydrous oxides, and metal phosphates and arsenates, for instance, which may be precipitated from their hydrosols by electrolyte-coagulation and filtered off from the bulk of the dispersion medium, may also give gels as the result of a relatively slight modification of the coagulation procedure, e.g., a change in the order or rate of mixing sol and electrolyte or a change in the concentrations or temperature at which coagulation occurs. Conditions are much the same for gels formed from ordinary solutions, as by double decomposition of inorganic electrolytes,<sup>22</sup> reduction in solubility by cooling or addition of non-solvent, etc. In these cases, however, the sol is a transient state, which may be so short-lived as to be experimentally undetectable.

Sol-gel transformations are often brought about by alteration in concentration of the disperse phase or in temperature of the system. In many instances it is sufficient merely to shake or stir the gel to convert it into a liquid sol, with the system returning in the course of time to the gel form when the mechanical treatment is stopped. One of the classical examples of such thixotropic behavior is the ferric oxide sol, which when treated with a small quantity of electrolyte, sets to a gel form. This gel can be liquefied by shaking and returned to gel on cessation of the treatment. Such *thixotropy* was first investigated systematically by Szegevari and Schalek.<sup>23</sup>

<sup>22</sup> Extensively studied by von Weimarn, footnote 11, p. 655.

<sup>23</sup> *Kolloid-Z.*, **32**, 318 (1923); **33**, 326 (1923).

Thixotropic properties are common in gels and in paste-like structures. They appear in gels produced by temperature changes as well as in those formed by the addition of electrolyte coagulant. Bentonite and other clay suspensions are notorious in their ability to form pastes which show pronounced thixotropy.<sup>24</sup> Such sols which contain rod-like or plate-like particles may be caused to set more rapidly to the gel form by any mechanical means which will facilitate the orientation of the particles. This phenomenon is known as *rheopexy*,<sup>25</sup> a term meaning solidified.

The coagulation of strongly lyophilic sols may take place in such a way that two liquid phases are formed, one rich and one poor in dispersed phase. de Jong and Kruyt<sup>26</sup> have called this particular type of coagulation process by the name *coacervation*. According to them it is essentially a discharging process in which the particles are not fully desolvated. In the sol condition the particles are stabilized by zeta potential and solvation, but in coacervation the second stability factor is not completely destroyed. Gelatin gels behave in this way on "salting-out" with sodium sulfate.

A large class of gels which is deserving of special mention may be formed by addition and condensation reactions to give the polymeric molecules of organic chemistry. They are the polyesters, polyamides and polyethers, the phenol-aldehydes, urea-aldehydes and glycerol-phthalic acid systems, etc. They have been already considered (pp. 648-651).

(68) **Theories of Gel Structure:** There are three general theories to explain the fact that a gel system which may consist largely of fluid actually behaves as a rigid solid. They are:

- (1) Solvation, i.e., immobilization of solvent by adsorption on the solute.
- (2) Presence of a three-dimensional network of solute.
- (3) Operation of long-range forces between solute particles.

Any one of them may be applicable to some gel systems, but not to others.

**Solvation:** Solvation is probably involved in the conditions for gel formation, but it is difficult to estimate its importance in the absence of unambiguous methods for measuring it. It is commonly said that the particles in hydrous ferric oxide sol, for instance, are more highly hydrated than those in arsenic trisulfide sol. The basis for the comparison, however, is not well defined, and it remains an open question to what extent differences ascribed to solvation are really due to differences in concentration, size of primary particles, degree of aggregation of primary particles, and the chemical properties of the stabilizing electrolytes. The uncertain function of solvation is illustrated by gelatin and dibenzoyl cystine, the former of which precipitates at the isoelectric point in a highly "hydrated" condition (85 to 90 per cent water), whereas dibenzoyl cystine precipitates in anhydrous form. In spite of its unsolvated condition,

<sup>24</sup> Freundlich and Sachs, *Kolloid-Z.*, **46**, 290 (1928).

<sup>25</sup> Freundlich and Juliusburger, *Trans. Faraday Soc.*, **31**, 920 (1935).

<sup>26</sup> *Proc. Acad. Sci. Amsterdam*, **32**, 839 (1929); *Kolloid-Z.*, **50**, 39 (1930).



dibenzoyl cystine forms jellies in much lower concentrations than does iso-electric gelatin.

The difficulty in estimating the significance of solvation is aggravated by uncertainty concerning the nature of the change leading to coagulation or gel formation in highly "solvated" colloids. Gelatin has been most frequently investigated, but no final conclusions have been reached. Some have assumed that a chemical change occurs upon cooling a gelatin sol, forming a new and insoluble substance that precipitates as a gel;<sup>1</sup> others believe that crystallization from a saturated solution occurs;<sup>2</sup> Fischer<sup>3</sup> considered the sol-gel change to be a phase reversal from a gelatin-in-water to a water-in-gelatin system; Ostwald<sup>4</sup> suggested that the gelation temperature is a critical solution temperature below which two essentially liquid phases separate; and Kraemer<sup>5</sup> pointed out the analogy between gelatin coagulation and the coagulation of Odén sulfur at a critical temperature. The nature of the changes initiating gelation upon cooling agar hydrosols or upon warming alcosols of nitrocellulose or sols of cellulose in cold sodium hydroxide is equally obscure.

A critical instability is a necessary but not a sufficient condition for gel formation. In addition there must be a sufficient concentration of dispersed phase, depending upon the particle size and shape, the aggregation habits of the dispersed material, and the amount of the dispersion medium adsorbed or otherwise bound by the gel structure. As a gel-forming sol is coagulated at increasing dilutions, a point is normally reached beyond which the coagulated phase fails to immobilize the entire liquid, and a gelatinous precipitate settles out. The minimum concentration for uniform gel formation is in a number of cases approximately a few tenths percent by volume, e.g., gelatin, agar, dibenzoyl cystine, silicic acid, manganese arsenate, some of the hydrous oxides, etc. In the case of fibrinogen, a volume fraction of as little as  $3 \times 10^{-5}$  suffices for gelation.<sup>6</sup> The ease with which such very dilute gels can be formed appears to be greatest when the colloidal substance is very highly dispersed and the stability conditions can be critically adjusted in the range of "slow" coagulation. The ordinary hydrosols of the metals, arsenic trisulfide, selenium, silver halides, and other salts, with volume concentrations much below 1 per cent are evidently too dilute to give gels. In addition their dispersities are usually low, compared to gelatin for instance, and their "slow" coagulation is not easily controlled.

In relatively high concentrations, conditions for gel formation are less restricted. The precipitates formed from dilute dispersions are relatively bulky products, which therefore have a rather high content of enclosed liquid. If the concentration of the sol approaches that of a gelatinous precipitate from a dilute sol, the lower fluidity of the concentrated system and the smaller dis-

<sup>1</sup> Smith, *J. Am. Chem. Soc.*, **41**, 135 (1919); Davis and Oakes, *ibid.*, **44**, 464 (1922); Wilson and Kern, *ibid.*, **44**, 2633 (1922); Lloyd, *Biochem. J.*, **14**, 147 (1920).

<sup>2</sup> von Weimarn, *op. cit.*; Bradford, in Alexander, *Colloid Chemistry*, Vol. I, chap. 47.

<sup>3</sup> *Soaps and Proteins* (New York: John Wiley and Sons, Inc., 1921).

<sup>4</sup> *Die Welt der vernachlässigten Dimensionen* (1922), p. 74.

<sup>5</sup> *J. Phys. Chem.*, **29**, 1169 (1925); **31**, 764 (1927).

<sup>6</sup> Ferry and Morrison, *J. Am. Chem. Soc.*, **69**, 388 (1947).

tances between particles permit the formation of a gel without the necessity of adjusting the instability to a critical value.<sup>7</sup> For instance, the gelatinous precipitate from dilute isoelectric gelatin contains 12 to 15 per cent gelatin, but an 8 to 10 per cent isoelectric gelatin gives a uniform jelly without any marked increase in Tyndall intensity. The mechanical rigidity and elasticity require a change in the positions and surface conditions of such a small proportion of the particles that other properties are practically identical in the sol and in the gel. A carefully studied case of this kind is that of sodium oleate, which Laing and McBain<sup>8</sup> found to have the same electrical conductivity, vapor pressure, sodium-ion activity and Tyndall intensity in sol and gel states.

Spatial conditions in concentrated dispersions may be more easily visualized by considering the sizes and shapes of the spaces between the particles. Coarse dry powders (sand, etc.) ordinarily pack to a volume concentration of approximately 50 per cent, which roughly corresponds to cubic packing of equal-sized spheres. Owing to static friction between particles and arching effects, very fine particles ordinarily pack less compactly. If the particles are immersed in a liquid that wets them, the films that separate the particles are not quickly squeezed out because of the appreciable viscous resistance, which is normal to thin films, and because of the low stresses tending to press the particles together. In a 6.5 per cent by volume dispersion of uniform spheres in cubic arrangement, the thickness of the films between adjacent spheres is equal to their diameter. If the particles are five  $m\mu$ , corresponding to hemoglobin molecules, or even 10 to 100  $m\mu$ , corresponding to common lyophobic sols, it is evident that the capillary spaces in a 6.5 per cent by volume dispersion are exceedingly fine. Relatively few particles need to adhere in order to immobilize the entire dispersion, and the rigidity of the structure will usually suffice to prevent closer packing. In such concentrations gel formation becomes the rule, and precipitates with supernatant liquid become the exception. In spite of its qualitative nature and obvious shortcomings, von Buzagh<sup>9</sup> and du Noüy<sup>10</sup> continue to interpret gelatin in terms of this theory.

*Three-dimensional Network:* There is at present almost universal acceptance of the view that gels possess a ramifying, more or less coherent, framework that retains the liquid component and confers rigidity and elasticity upon the system as a whole. The earlier concepts of a "brush-heap" or "ramifying aggregates" have been made more exact by the recent work of Flory<sup>11</sup> and Stockmayer<sup>12</sup> in their studies of the conditions for the formation of three-dimensional networks from molecules or particles carrying reactive groups which combine with each other, and by the kinetic theories of elasticity of Guth<sup>13</sup> and of Flory<sup>14</sup>

<sup>7</sup> Many of the gels prepared by von Weimarn, *op. cit.*, belong to this group.

<sup>8</sup> *J. Chem. Soc.*, **117**, 1506 (1920); *Nature*, **125**, 125 (1930).

<sup>9</sup> *Colloid Systems* (London: Technical Press, 1937).

<sup>10</sup> *Studies in Biophysics* (New York: Reinhold Publishing Co., 1945).

<sup>11</sup> *J. Am. Chem. Soc.*, **63**, 3083, 3091, 3097 (1941); *Chem. Rev.*, **39**, 137 (1946).

<sup>12</sup> *J. Chem. Phys.*, **11**, 45 (1943); **12**, 125 (1944).

<sup>13</sup> James and Guth, *J. Chem. Phys.*, **11**, 455 (1943).

<sup>14</sup> Flory and Rehner, *ibid.*, **11**, 513 (1943).

and their associates in which it is postulated that a network of flexible strands resists deformation because a decrease in entropy would be thereby involved.

By his statistical theory Flory showed that when polyfunctional molecules react, a branched network which is infinite in extent will suddenly appear as the reaction proceeds to give a gel system. This point, measured by the proportion of groups which has reacted, can be calculated in terms of the proportion of polyfunctional molecules present and their functionality. At the gel-point the reaction is still far from completion, and more and more of the smaller molecular kinetic units become attached to the network until its relative mass or gel fraction eventually approaches unity. Even in this condition the reaction is not completed because network strands may react with each other to give additional cross-links with an attendant increase in rigidity of the gel.

A similar structural arrangement may be obtained by the use of chemical reagents which cause cross-linking of linear molecules. Thus, the long molecules of raw rubber form a network and therefore a gel on vulcanization. Actually Flory<sup>15</sup> has shown that the number of cross-links in such a structure (butyl rubber) can be calculated in three ways: (a) from measurements of the properties of insoluble (gel) and soluble (sol) material in samples of different initial molecular lengths; (b) from the elastic modulus of the unswollen rubber; (c) from the maximum amount of liquid imbibed by the gel in equilibrium with pure solvent.

Interesting calculations have been made to describe some of the properties of network gels. Among them are the location of the gel-point, the molecular weight distribution, the nature of the sol-gel transformation, the rigidity of the gel, and the extent of possible swelling.<sup>16</sup>

*Long-range Forces:* Optical and X-ray studies indicate that in certain gels long-range forces between the solute particles operate to hold them in a stable and regular array, with relatively long distance spacing between them.<sup>17</sup> A typical and well-studied example is the tobacco mosaic virus protein, the molecules of which are rod-like in shape. Bernal and Fankuchen have shown<sup>18</sup> that in aqueous solution they may exist in several different states of aggregation, depending upon the solution concentration. In the concentration range of 13 to 100 per cent dry virus protein a gel is formed in which a hexagonal array of the protein molecules determines the structure. The X-ray analysis shows that the lattice is two dimensional, with no regularity in the direction of the axes of the molecule.

**(69) Formation of Gels:** There are two different mechanisms by which gels may be formed, although it is not always possible to determine in a particular case which is involved. In one case, conditions are changed so that the dis-

<sup>15</sup> *Chem. Rev.*, **35**, 51 (1944).

<sup>16</sup> See review articles by Flory, *Chem. Rev.*, **39**, 137 (1946), and Ferry, *Advances in Protein Chemistry*, IV (New York: Academic Press, 1948).

<sup>17</sup> These long range forces have been shown by Onsager to be due to rotational Brownian movement effects (*Ann. N. Y. Acad. Sci.*, **51**, 627 (1949)).

<sup>18</sup> *J. Gen. Physiol.*, **25**, 111 (1941).

solved or dispersed solute is no longer soluble, and it begins to precipitate or coagulate. Conditions of precipitation must be such that it does not occur too rapidly, and furthermore the precipitate must not be so lyophobic as to shrink quickly to a coherent, compact mass. It seems that certain elements or parts of the precipitating material must maintain a certain affinity for the solvent, so that a brush-heap structure may develop, with a relatively few points of union between crystalline fibrils, strong enough, however, to support the framework structure as long as the framework is buoyed up by the liquid. At the same time, depending upon the strength of the framework, there must be a certain minimum concentration, otherwise the framework will collapse and a separate precipitate will form. Electron microscope pictures reveal the very fine and very long fibrils in soap gels, and many other gels would probably be seen to have a similar structure if examined in this way.

Dibenzoyl cystine gel is a good example of a gel with intermeshing crystals. It is made by dissolving the dibenzoyl cystine in hot 95 per cent alcohol and then adding a large volume of hot water. In several hours, a rigid gel will form, although in a few days, continued crystallization leads to shrinkage of the gel, with exudation of liquid ("syneresis") and then white nuclei of radiating crystal needles appear. Finally, the entire amount of dibenzoyl cystine will be in well-defined crystal form with only a supernatant liquid and no gel. A manganese arsenate gel of suitable composition behaves similarly, but more slowly. For silica gel, it may be presumed that the gel fibers are polymeric silicic acid, which may in a very long time finally go over to crystalline silica, although many of them show extensive syneresis. Owing to the appreciable difference in refractive index of water and silicic acid, and perhaps also, the appreciable particle size, silica gels are almost always somewhat turbid. Even a gelatinous barium sulfate can be obtained from highly concentrated solutions of  $\text{Ba}(\text{CNS})_2$  and  $\text{MnSO}_4$  (5 to 7M). Here, however, the conditions are such as to give very fine crystals in such large volume that the mixture is a solid mush. Many gels can be also made by change of solvent or reduction of solubility by lowering of temperature, e.g., from soaps in oils.

High molecular weight materials also may form gels by precipitation of the dispersed material by change of solvent or temperature (when the solubility coefficient is large). Gelatin gels belong in this category. At about 30°C, some sort of reversible tautomeric change occurs to give a product of very low solubility at lower temperature, and the precipitation leads to a gel. Comparison of the effect of pH on gel formation and turbidity shows that gelation occurs just adjacent to the conditions corresponding to optimum precipitation. Thus, gelation represents a balance between precipitation and solution—a critical condition of incipient precipitation, as it were.

Agar also forms gels due to marked change in solubility with temperature. It shows a curious property in that the temperature of melting of the gel is 20° or so higher than the temperature of gelation. The differential for gelatin is quite small.

Cellulose nitrate and acetate also give temperature-reversible gels in special

solvents. For instance, the nitrate in a mixture of amyl acetate and petrol ether gels on raising the temperature; the acetate in benzyl alcohol gels on cooling. Certain nitrates also dissolve in methyl alcohol at low temperatures, but gel upon heating. Methyl cellulose in water shows the same behavior. All these illustrate temperature-reversible gelation. Pectin, the gelating substance in table (fruit) jelly, is another example. In general, these gels that form when the temperature is changed depend upon marked variation in solubility, and the gel formation is reversible. Obviously, when gelation involves a change of solvent, the gelation is not directly reversible. The same is true of gels formed by chemical reaction giving an insoluble product, like silica gel, manganese arsenate gel; the gelation of viscose by heat or by chemical means, the gelation of egg albumin by heat, etc.

(70) **Mechanical Properties of Gels:**<sup>1</sup> Many of the mechanical properties peculiar to gels are easily interpreted qualitatively by consideration of their heterogeneous structure. Gels with a high liquid content possess a low rigidity and a low elastic limit. Poisson's ratio is practically equal to 0.5, as for liquids, which means that deformation takes place without appreciable change in volume. Hooke's law is usually obeyed only at low extensions. Deformations often require considerable time for their completion. Not infrequently the strain continues as long as the gel is stressed; that is, weak gels are to a certain extent plastic solids. A number of investigators<sup>2</sup> believe that these properties are due to the existence of a gel structure formed of elastic elements, the displacements of which are retarded by the viscous drag of the surrounding liquid.

The most characteristic property of a gel is its modulus of rigidity. It is calculated from measurements of the deformation of a gel in shear and in extension, respectively, under known stress<sup>3</sup> or of the velocity of propagation of transverse vibrations.<sup>4</sup> It is a function of the several variables which define the system. Thus, in the case of gelatin gels the rigidity is approximately proportional to the square of the gelatin concentration over a considerable range of concentrations; it decreases markedly with the decrease in gelatin molecular weight produced by hydrolysis; added reagents which lower the melting point of the gel also diminish the rigidity, etc.

(71) **Optical Properties of Gels:**<sup>1</sup> Gels normally become birefringent when

<sup>1</sup> Freundlich, *Colloid and Capillary Chemistry* (1926), p. 716. Gelatin: Leick, *Ann. Physik*, **14**, 139 (1904); Rohloff and Shinjo, *Physik. Z.*, **8**, 442 (1907); Sheppard, *et al.*, *J. Am. Chem. Soc.*, **44**, 1857 (1922); *Ind. Eng. Chem.*, **16**, 593 (1924); Freundlich and Seifriz, *Z. physik. Chem.*, **104**, 233 (1923); Scarth, *J. Phys. Chem.*, **29**, 1009 (1925). Cellulose acetate: Mardles, *Trans. Faraday Soc.*, **19**, 118 (1923). Cellulose acetate and gelatin: Poole, *ibid.*, **21**, 114 (1925); **22**, 82 (1926). Starch: Peirce, *J. Textile Inst.*, **19**, T237 (1928). Wool: Shorter, *ibid.*, **15**, T219 (1924); **18**, T78 (1928); Speakman, *ibid.*, **17**, T457 (1926). Flax: Matthews, *ibid.*, **18**, T207 (1928).

<sup>2</sup> See, for instance, Poole, *loc. cit.*

<sup>3</sup> Hatschek and Jane, *Kolloid-Z.*, **39**, 300 (1926).

<sup>4</sup> Ferry, *Rev. Sci. Instruments*, **12**, 79 (1941).

<sup>1</sup> Freundlich, *op. cit.*, p. 720; Ambronn and Frey, *Das Polarisationsmikroskop* (Leipzig: Akademische Verlagsgesellschaft m. b. h., 1926). Gelatin: Leick, *loc. cit.*; Quincke, *Ann. Physik*, **14**, 849; **15**, 1 (1904); Hatschek, *Kolloid-Z.*, **28**, 210 (1921); **35**, 67 (1924); **36**, 202

deformed.<sup>2</sup> Three different conditions, either singly or together, may be responsible for the anisotropy: (1) variations in density due to tension and compression, such as cause the negative birefringence of compressed homogeneous isotropic solids; (2) the presence of more or less oriented, non-spherical, isotropic particles in a medium having a different refractive index;<sup>3</sup> and (3) oriented anisotropic particles. Quantitative studies of the induced double refraction in various gels and under a variety of conditions clearly show that all three effects actually occur, but it is not easy to determine their relative importance. It seems certain that many of the naturally occurring organic xerogels contain oriented anisotropic particles.

*Nägeli's Micellar Theory:* The botanist Nägeli<sup>4</sup> was one of the earliest to study the double refraction of xerogels thoroughly and to realize its significance. The form of organic structures, such as starch, cellulose, proteins, etc., and their mechanical properties, birefringence, and behavior upon imbibing liquids led Nägeli to conclude that these structures are built up of submicroscopic, water-insoluble, birefringent crystallites, which he called micelles. The macroscopic anisotropy in mechanical and optical properties he assumed to be due to a regular orientation of the micelles. An imbibed liquid was supposed to enter the intermicellar spaces, separating the micelles and reducing the cohesion of the swollen body. When complete dispersion occurs, the dispersed units, according to Nägeli, are micelles, not molecules. Under favorable conditions the dispersed micelles unite to form a ramifying jelly structure.

*X-ray Analysis of Natural Xerogels:* Nägeli's theory attracted relatively little attention, in spite of the further development and confirmation that it received from Ambronn and his school, until modern X-ray crystal-structure analysis gave a more detailed picture of the nature of the crystallites.<sup>5</sup> Although still in the stage of active development and refinement, the new methods have already yielded results of great importance.

The structure of cellulose (ramie) has been most completely worked out. As a result of the investigations of Herzog, Polanyi, Sponsler, Meyer and Mark, and their co-workers,<sup>6</sup> it is now relatively certain that celluloses, whether from

(1925); Sheppard and McNally, *Colloid Symposium Annual* (1930), p. 17. Cellulose acetate and nitrate: Wächter, *Fortschr. Mineral. Krist. Petr.*, **12**, 119 (1927); McNally and Sheppard, *J. Phys. Chem.*, **34**, 165 (1930).

<sup>2</sup> Because of the difficulty of eliminating accidental strains a truly isotropic gel is in reality a rarity.

<sup>3</sup> Theoretically discussed by Wiener, *Abhandl. Sächs. Akad. Wiss. Leipzig*, **32**, No. 6 (1912).

<sup>4</sup> *Die Stärkekörner* (Zürich: 1858), and later books; *Die Micellartheorie*, Ostwald's Klassiker, No. 227. See also Katz, *Micellartheorie und Quellung der Zellulose*, in Hess, *Die Chemie der Zellulose* (Leipzig: Akademische Verlagsgesellschaft m. b. h., 1928), pp. 605-769.

<sup>5</sup> Nishikawa and Ono, *Proc. Phys. Math. Soc., Japan*, **7**, No. 8 (1913), using hemp and silk, were the first to obtain evidence by X-ray analysis for the presence of crystalline material in organic xerogels. See also, p. 656.

<sup>6</sup> Herzog, Jancke, and Polanyi, *Z. Physik*, **3**, 343 (1920); Polanyi, *ibid.*, **7**, 149 (1921); Herzog and Jancke, *Z. physik. Chem.*, **139**, 235 (1928); Sponsler and Dore, *Fourth Colloid Symposium* (1926), p. 174; Meyer and Mark, *Ber.* **61**, 593 (1928); Mark and Meyer, *Z. physik. Chem.*, **2B**, 115 (1929); Mark and Susich, *ibid.*, **4B**, 431 (1929); Andress, *ibid.*, **136**, 279 (1928); **2B**, 380 (1929); **4B**, 192 (1929); Hauser, *Ind. Eng. Chem.*, **21**, 124 (1929).

plant or animal sources, consist largely of microcrystalline material the unit cell of which is monoclinic with the following dimensions:  $a = 8.3 \text{ \AA}$ ;  $b = 10.3 \text{ \AA}$ ;  $c = 7.9 \text{ \AA}$ ;  $\beta = 84^\circ$ . In ramie, the crystallites are oriented with the  $10.3 \text{ \AA}$  dimension parallel to the fiber axis; in cotton the arrangement is spiral. Each unit cell is supposed to contain two cellobiose groups ( $\text{C}_{12}\text{H}_{20}\text{O}_{10}$ ) parallel to the length of the cell, one through the center of the cell, and one on each edge and shared by the three adjacent cells. The glucose residues are probably in the form of 1:5 rings bridged together not only within a single cell but between adjacent cells along the fiber axis by 1:4 glucosidal oxygen bridges. In other words, the crystals are believed to consist of long primary-valence chains of glucose residues arranged parallel to the fiber axis and held together laterally by the type of secondary valence usually operative between molecules in a crystal. The size of the crystallite or micelle is rather uncertain and undoubtedly varies from case to case; in native ramie it has been estimated to be 30 to 50  $\text{\AA}$  thick and 300 to 500  $\text{\AA}$  long.<sup>7</sup> If the chain molecule is the full length of the micelle, its "molecular" weight is ca. 10,000 to 15,000. Because of the great cohesion between molecules, however, it is unlikely that a micelle can be separated into single molecules without disrupting the molecules themselves.

When cellulose or hydrated cellulose imbibes water, the water enters the intermicellar spaces, as supposed by Nägeli, and leaves the micelles unchanged.<sup>8</sup> On the other hand, the imbibition of water by inulin<sup>9</sup> or of some organic liquids by cellulose acetate<sup>10</sup> is intramicellar, the micelle lattice being expanded. In these cases the change is reversible, although a new structure appears if the triacetate is dispersed and reprecipitated. The imbibition of sufficiently concentrated alkali to cause mercerization leads to a permanent change in the crystallites, which are then typical of "regenerated" celluloses.<sup>11</sup> Mercerization leaves the length of the unit cell unchanged, as would be expected if the long chain molecules remained intact during the process. Nitration and acetylation give products with new crystallite structures, sometimes without modifying the unit cell dimension parallel to the fiber axis.<sup>12</sup> X-ray analysis gives no information concerning the fate of the crystallites when a xerogel is dispersed in a liquid, but judging from the absence of well-defined crystallites in some xerogels of cellulose nitrate or acetate or regenerated cellulose, one is tempted to assume that the micelle is so highly swollen, deformed, and perhaps disrupted that it can not easily return to its original state. It is, however, in some cases possible to facilitate the formation of crystallites or increase the extent of

<sup>7</sup> These conclusions are challenged by Hess and Trogus, *Ber.*, **61**, 1982 (1928); *Z. physik. Chem.*, **4B**, 321 (1929).

<sup>8</sup> Katz, *Physik. Z.*, **25**, 321, 659 (1924). Chitin and silk fibroin behave similarly.

<sup>9</sup> Katz and Mark, *ibid.*, **25**, 431 (1924).

<sup>10</sup> Hess and Trogus, *Z. physik. Chem.*, **5B**, 161 (1929).

<sup>11</sup> Katz and Mark, *Z. physik. Chem.*, **115**, 385 (1925); Katz and Hess, *ibid.*, **122**, 126 (1926); Herzog and Jancke, *ibid.*, **139**, 235 (1928); Andress, *ibid.*, **4B**, 190 (1929).

<sup>12</sup> Herzog and Náray-Szabó, *Z. physik. Chem.*, **130**, 616 (1927); Náray-Szabó and Susich, *ibid.*, **134**, 264 (1928); Hess and Trogus, *ibid.*, **5B**, 161 (1929).

orientation by stretching or otherwise mechanically working the gel while it is in a plastic state.<sup>13</sup>

The existence of microcrystalline micelles has been confirmed by X-ray analysis for a number of neutral polymeric substances, as silk fibroin,<sup>14</sup> chitin,<sup>15</sup> gelatin and collagen.<sup>16</sup> All of these probably contain chain molecules of high molecular weight. The work of Astbury and associates<sup>17</sup> with the fibrous proteins has been outstanding in spite of some elements of speculation. One of the important discoveries is the fact that these proteins appear to fall for the most part into two main configurational families, (a) the keratin-myosin-fibrinogen group and (b) the collagen group. In the keratin group the unit of structure is a polypeptide grid, the normal equilibrium configuration of which is buckled. The characteristic long range elasticity of this group is explained as being due to the ability of the chains to unfold and refold. The essential structural problem which remains is the exact nature of the intramolecular fold which characterizes the group.

Making use of the idea of the folding of chains derived from the X-ray study of the fibrous proteins, it is possible to think in terms of the structure of the so-called globular or corpuscular proteins, particularly as regards their characteristic tendency to denaturation,<sup>18</sup> an unfolding process. Thus, it has been demonstrated<sup>19</sup> that artificial fibrous proteins can be spun after the denaturation of many globular proteins.

Various synthetic chain molecules, such as the polyoxymethylenes resemble the natural materials in that they possess colloidal properties and a molecular length greatly exceeding the size of the unit cell of the crystalline state. The absence of crystallinity in macromolecular materials of the bakelite and glyptal type is due to the complicated and irregular three-dimensional extension of the molecules, which prevents the orientation necessary for X-ray interference effects.

A particularly interesting natural xerogel is rubber, which in its ordinary state gives no X-ray evidence of crystallinity. However, repeated stretching of it beyond the elastic limit until a permanent elongation of five to ten times is attained gives a fibrous product having a well-defined crystalline structure.<sup>20</sup>

<sup>13</sup> Silk and hydrated cellulose: Herzog and Jancke, *Z. Physik*, **52**, 755 (1929). Hydrated cellulose: Burgeni and Kratky, *Z. physik. Chem.*, **4B**, 401 (1929). Cellulose nitrate and acetate: Trillat, *J. phys. rad.*, **10**, 370 (1929).

<sup>14</sup> Brill, *Ann.*, **434**, 204 (1923); Herzog and Jancke, *loc. cit.*

<sup>15</sup> Gonell, *Z. physiol. Chem.*, **152**, 18 (1926); Meyer and Mark, *Ber.*, **61**, 1936 (1928).

<sup>16</sup> Katz and Gerngross, *Kolloid-Z.*, **39**, 180 (1926); Marks, Bear and Blake, *J. Exptl. Zoology*, **111**, 55 (1949).

<sup>17</sup> Astbury, *J. Text. Inst.*, **27**, 281 (1936); *Nature*, **137**, 803 (1936); *Advances in Enzymology*, **3**, 63 (1943).

<sup>18</sup> Neurath, Greenstein, Putnam, and Erikson, *Chem. Rev.*, **34**, 157 (1944).

<sup>19</sup> Lundgren, *J. Am. Chem. Soc.*, **63**, 2854 (1941); Lundgren and O'Connell, *Ind. Eng. Chem.*, **36**, 370 (1944).

<sup>20</sup> Katz, *Chem. Ztg.*, **49**, 353 (1925); Hauser and Mark, *Kolloid-chem. Beih.*, **22**, 63; **23**, 64 (1926); Meyer and Mark, *Ber.*, **61**, 1939 (1928); Mark and Susich, *Kolloid-Z.*, **46**, 11 (1928); Hauser, *Ind. Eng. Chem.*, **21**, 249 (1929); Katz, *Kautschuk*, **5**, 6 (1929).



Upon being warmed or swollen (see below), the crystallites spontaneously disappear and the broad X-ray interference ring characteristic of amorphous bodies reappears. The old theory of long coiled molecules<sup>21</sup> has been offered as an explanation of this behavior; the coiled-up molecules are presumably straightened by the stretching process and packed together with the regularity of spacing and arrangement necessary for a definite crystalline pattern by X-ray analysis. The length of the unit cell corresponds to two isoprene groups; the rubber molecule is supposed to consist of a large number of isoprene groups linked together in a chain by primary valence. According to Fikentscher and Mark,<sup>22</sup> the  $\text{CH}_2$ -groups of each isoprene residue occupy *cis*-positions relative to each other. On account of the rigidity of the double bonds and steric hindrance effects, such a chain molecule tends spontaneously to coil up in order to relieve the strain between carbon atoms. A spiral molecule also provides an explanation for the unusual mechanical properties of rubber.

(72) **Desiccation of Gels:** The distinctions expressed by the classification of sols into lyophiles and lyophobic are also evident in their gels. Upon evaporation of the dispersion liquid from a typical lyophilic gel the fall in vapor pressure and in liquid content traces an S-curve (Type II, Fig. 27). The volume of the gel continuously decreases until a horny residue is obtained, which has almost as small a specific volume as the dispersed phase in the original sol.<sup>1</sup>

The loss of liquid from lyophobic gels, exemplified by the hydrogels of silica and the hydrous oxides of the metals, is somewhat more complicated.<sup>2</sup> In the case of silica gel, for instance, the vapor pressure, liquid content, and volume of gel all gradually become smaller, much as in a lyophilic gel, until the gel contains about two moles of water to one of silica, or about 40 per cent by volume of silica.

A lyophilic gel may be converted to a lyophobic one by a suitable change of the liquid component, whereupon desiccation proceeds in the manner typical of lyophobic gels, giving a rigid, porous xerogel. The conversion of lyophilic gelatin hydrogel, for instance, may be brought about by extraction of the water with a series of mixtures of water and a liquid, e.g., alcohol, in which gelatin does not disperse, the concentration of water gradually being reduced to zero.<sup>3</sup>

(73) **Imbibition and Swelling:**<sup>1</sup> The contrast between lyophobic and lyophilic behavior in gels is more strikingly shown by imbibition than by desiccation.

*Lyophobic Imbibition:* A lyophobic xerogel, e.g., silica gel, imbibes any liquid that wets the gel. The maximum volume taken up, in the absence of chemical

<sup>21</sup> Ditmar, *Der Kautschuk* (Berlin: Springer, 1912), p. 47.

<sup>22</sup> *Kautschuk*, 6, 2 (1930).

<sup>1</sup> Katz, *Kolloidchem. Beih.*, 9, 70 (1917).

<sup>2</sup> The classical investigations are by van Bemmelen, *Die Absorption* (1910). Similar studies, particularly on silica gel, were made by Zsigmondy and his co-workers (1911-14), using vacuum methods of desiccation; the references and the essential results are given in his *Kolloidchemie* (3d ed.; 1920), p. 213 ff.

<sup>3</sup> Bachmann, *Z. anorg. Chem.*, 100, 1 (1917).

<sup>1</sup> Katz, *Ergebn. exakt. Naturwiss.*, 3, 316 (1924); 4, 154 (1925).

reactions or foreign gases, is dependent primarily on the volume of the pores in the xerogel, for only a slight swelling, if any, accompanies imbibition.<sup>2</sup> In other words, the desiccation of a dilute lyophobic gel is irreversible.

Porous xerogels obtained from lyophilic gels (see above) behave similarly towards non-peptizing liquids, imbibing them, without swelling, in amounts determined by the porosity.<sup>3</sup>

Reference has already been made (p. 594) to the adsorption of vapors by porous xerogels. In connection with structure, the capillary character of the adsorption is particularly significant. Upon the assumption that the adsorbed vapor at medium and high relative pressures is condensed to a liquid within the gel pores, Kelvin's equation for the change in vapor pressure of a liquid in capillaries can be used to estimate the effective pore diameter at various stages of adsorption. In a typical silica gel Anderson<sup>4</sup> found the apparent pore diameter at the turbidity point to be about  $2.6 \mu$  for water, alcohol, and benzene. Although it is questionable if Kelvin's equation is accurate for such small pores, the agreement obtained with liquids having such different surface tensions as water and benzene supports the capillary interpretation of the adsorption. The close relation between the surface tensions and heats of wetting (cf. Patrick's theory, p. 608) also confirms Zsigmondy's conclusion of a submicroscopically porous structure in the silica gel. Other lyophobic xerogels undoubtedly have similar structures.

*Lyophilic Imbibition:* The dissolution of macromolecular substances, i.e., natural colloids, does not take place simply by the escape of molecules from the solid surface into the solvent medium, as is the case for the common crystalline substances. Instead, the medium penetrates into the interior of the solid colloid or xerogel, at the same time causing it to swell.<sup>5</sup> The factors that determine whether a certain colloid will imbibe a specific liquid are much the same as determine solubility in general; they were referred to in connection with the formation of lyophilic sols. It may be assumed that swelling occurs if the adhesional or solvation energy for the particular xerogel and liquid is greater than the cohesive energy of the gel, at least at some regions in the gel. Because of the variety of chemical groups that may be present in a macromolecular gel, the cohesive energies and the adhesional energies toward a given liquid (not necessarily a single compound) may vary from point to point in the gel, at some points the adhesional energy and at other points the cohesive energy being the greater. If the adhesional energy is superior at a sufficient number of points in the xerogel, swelling is "unlimited," leading eventually to disintegration of the xerogel into microscopic or submicroscopic pieces, i.e., to the formation of a sol.<sup>6</sup> This is the case for gelatin or agar in hot water, gelatin in cold concentrated potassium iodide solution, nitrocellulose in acetone, and

<sup>2</sup> McBain and Ferguson, *J. Phys. Chem.*, **31**, 564 (1927).

<sup>3</sup> Alcohol and benzene in porous gelatin, Bachmann, *Z. anorg. Chem.*, **100**, 1 (1917).

<sup>4</sup> *Z. physik. Chem.*, **88**, 191 (1914); see also Bachmann, *loc. cit.*

<sup>5</sup> See below for X-ray analyses of the swelling process.

<sup>6</sup> Kraemer and Williamson, *J. Rheology*, **1**, 76 (1929).

cellulose in cuprammonium solution. If the cohesive energy is greater at every or almost every point, no appreciable imbibition takes place, and the behavior is lyophobic. Such is the case for gelatin and benzene, rubber and water, nitrocellulose and heptane. In intermediate cases a limited degree of swelling occurs, the magnitude of which depends upon the imbibition potential and the elastic constraints imposed by the cohesion of the gel.

The constraints often reflect the history of the gel. For instance, Arisz<sup>7</sup> observed that gelatin xerogels prepared by drying out gels of various concentrations rapidly swell in water to the original volumes, beyond which swelling is relatively slow. The cohesion of a gel can in some cases be reduced by mechanical treatment; e.g., rubber can be broken down by milling so that swelling in benzene continues until a sol is formed. Repeated swelling and de-swelling also commonly change (usually decrease) the cohesion of a gel.

The imbibition potential appears to depend principally upon two factors: (1) the combination of gel and swelling liquid to form what may be called solvates or adsorption compounds and (2) the osmotic pressure of diffusible constituents retained within the gel by electrical forces or by the semipermeable quality of the gel structure itself. The swelling of isoelectric gelatin and other proteins in water, of vulcanized rubber in benzene, and of other organocolloids in nonaqueous media represents the effect of solvation although in many of these cases an osmotic-pressure effect probably also plays some part on account of the nonhomogeneity of the gel substance. Many of the polymeric colloids (both natural and artificial) contain relatively low molecular-weight material that dissolves in the swelling medium within the gel but is prevented from escaping to the outside by the gel structure.<sup>8</sup>

*Procter-Wilson Theory:* In the presence of electrolytes, the combination of specific ions with the colloid and the prevention of diffusion of the product from the gel lead to an accumulation of diffusible ions and a greater osmotic pressure within the gel.<sup>9</sup> Osmosis into the gel accordingly occurs until the elasticity of the gel balances the difference in osmotic pressures. This swelling factor has been successfully worked out in considerable detail by Procter and Wilson<sup>10</sup> for the swelling of gelatin and collagen in electrolyte solutions. By combining the empirical results for the acid- or base-combination of gelatin with Donnan's theory of membrane equilibria (cf., p. 524), which describes the distribution of diffusible ions inside and outside the gel and the resulting osmotic-pressure differences, it may be predicted that the swelling tendency, as far as this factor is concerned, should be zero at the isoelectric point, that it should rise to a maximum at a pH about 3, regardless of the acid used, and that it should then fall toward zero at low pH's. The swelling tendency should be approximately

<sup>7</sup> *Kolloidchem. Beih.*, 7, 1 (1915).

<sup>8</sup> The swelling of isoelectric gelatin is discussed from this point of view by Northrop and Kunitz, *J. Gen. Physiol.*, 10, 161 (1926-27).

<sup>9</sup> Procter, *Kolloidchem. Beih.*, 2, 270 (1911).

<sup>10</sup> Procter and Wilson, *J. Chem. Soc.*, 109, 307 (1916); see also, Loeb, *Proteins and the Theory of Colloidal Behavior* (1926).

the same for all strong acids of a given valence type and inversely proportional to the basicity of the acid. Neutral salts should repress the swelling, the effectiveness being greater for polyvalent anions. The swelling of gelatin actually accords with these predictions to a considerable extent, so that in this particular case the Donnan osmotic-pressure effect appears to dominate in determining the swelling. Loeb and his co-workers have contributed a large body of experimental results supporting the theory and leading to its extension. They have conclusively demonstrated the occurrence of Donnan membrane effects in dispersions of proteins in aqueous electrolyte solutions. They have shown that the specific differences in the degree of swelling of protein gels in various dilute electrolytes, which give rise to the "Hofmeister ion-series," are largely due to differences in pH of the solutions. They have also shown that the Procter-Wilson theory of swelling provides an explanation of the parallelism<sup>11</sup> with change in pH between the changes in the swelling of gelatin gels and the viscosity of dilute gelatin dispersions (at 20 to 25°C), if it is assumed that the dilute dispersions contain submicroscopic gel particles that change in their degree of swelling with pH like ordinary gels.

The Donnan effect is not, however, the only factor controlling the swelling of protein gels. At the isoelectric point, gelatin swells in water to 7 or 8 times its volume although the Donnan effect is zero; on each side of the isoelectric point the Donnan effect is superimposed on the factor operating at the isoelectric point. In dilute solutions of certain salts, e.g., potassium iodide, and in most concentrated electrolyte or nonelectrolyte solutions, differences in the degree of swelling of gelatin are also due in part to changes in the cohesion of the gel structure, which can not be predicted from the Procter-Wilson theory. This theory is of course not at all applicable to the large body of gels that swell in nonaqueous, electrolyte-free liquids.

*Swelling Pressure and Heat of Swelling:* During the first stages of swelling of a xerogel, a considerable pressure is developed. The swelling of dried wooden wedges has been used since antiquity for exerting large mechanical forces over small distances.<sup>12</sup> According to Posnjak,<sup>13</sup> the swelling pressure increases approximately as the cube of the gel concentration. The initial pressure obtainable with a well-dried xerogel is difficult to measure; for gelatin in water, it is estimated to be several thousand atmospheres.

The swelling-pressure equilibrium is usually considered to be a true equilibrium suitable for thermodynamic analysis, although considerable caution must be exercised in making predictions concerning gel behavior therefrom. The usual isothermal, reversible cycle of transfers of swelling liquid between two gels swollen to different extents but otherwise identical yields the result

<sup>11</sup> The parallelism is a transient one that occurs upon cooling the gelatin dispersions from above 35 to 40°C and soon disappears below 25°C (Kraemer and Fanselow, *Fourth Colloid Symposium* (1926), p. 110).

<sup>12</sup> The pressure is exerted only by the gel; the total volume of gel and liquid decreases during imbibition, Freundlich, *Colloid and Capillary Chemistry*, p. 714.

<sup>13</sup> *Kolloidchem. Beth.*, 3, 417 (1912).

that the swelling pressure  $P$  is related to the relative vapor pressure  $h$  of the liquid, its molecular weight  $M$ , and its specific volume  $v$  by the expression,<sup>14</sup>

$$P = - \frac{RT}{Mv} \ln h \quad (73.1)$$

No data are available for testing the accuracy of the equation.

Swelling is generally accompanied by an evolution of heat. The initial differential heats of swelling for various dry proteins and carbohydrates fall in the range 200 to 400 cal/g of gel.<sup>15</sup> The differential heat of swelling decreases with increasing swelling.<sup>16</sup> In some cases the difference in the free energies of two gels at different degrees of swelling is approximately equal to the difference in heat contents, as estimated from calorimetric measurements of the heat of swelling. This means that a swelling gel under ideal conditions can convert potential energy into mechanical work with practically 100 per cent efficiency. Such gels are in this respect like "ideal concentrated solutions," such as aqueous sulfuric acid and some other solutions having large positive heats of dilution.<sup>17</sup> Katz offers this fact in support of the view that the relation between a gel and a swelling liquid is the same as that between solute and solvent in an ordinary solution. Although this may well be the case, it is rather unlikely that gels are generally "ideal" systems.

A thermodynamic relation of the Clausius-Clapeyron type may be set up for the relation between the heat of swelling and the temperature coefficient of swelling. The relation is however of limited significance, for two gels with the same composition but at different temperatures are often not in thermodynamically comparable states. In the case of gelatin, for instance, the positive heat of swelling and a careless application of thermodynamics might lead one to conclude that swelling should decrease with rising temperatures. On the contrary, in the range of ordinary temperatures, the equilibrium (pseudo-equilibrium?) values for the swelling of gelatin increase with temperature. With increasing temperature the gel structure is more completely peptized so that a greater swelling occurs even with a smaller imbibition potential. Differences in gel structure due to previous history, i.e., hysteresis effects, also often prevent a satisfactory thermodynamic analysis of swelling.

General mention has been made of the special, yet very important, type of gelation in which a three-dimensional molecule of near infinite size is produced by chemical means with the result that the whole system is immobilized. Rubber cement may be gelled, for instance, by means of sulfur chloride, a vulcanization and cross linking occurring to produce one molecule filling the entire space available. Polymerization of styrene containing a small amount of divinyl benzene (a cross-linking agent) leads also to gels. So also do the heating of certain unsaturated oils, like tung oil, or the extensive reaction under

<sup>14</sup> Katz, *ibid.*, 9, 1 (1917).

<sup>15</sup> Freundlich, *op. cit.*, p. 682.

<sup>16</sup> Cf. a similar change in heat of adsorption with increasing adsorption, p. 610.

<sup>17</sup> Nernst, *Theoretische Chemie* (8th-10th ed.; Stuttgart: Enke, 1921), p. 170.

proper conditions of a phenol-formaldehyde or other resin-forming reaction mixture. In general, a reaction mixture containing a suitable amount of a tri- or higher functional reactant can lead to three-dimensional molecules of unlimited size. Some of the reactions are special in character, for instance with formation of a heavy bi- or trivalent metal salt, as with Cu, etc., with nitro-cellulose containing free acid groups.

### EMULSIONS AND AEROSOLS

(74) **Emulsions:**<sup>1</sup> In some respects the study of emulsions is one of the most interesting subjects in colloid science. Also, the great importance of emulsions in many technical processes is so well known that it is hardly necessary to mention applications to the leather, wool, rubber, tar, paint, food, insecticide, laundry and emulsion polymerization industries. A basic distinction is made in types of emulsion, the two being oil in water (O-W) and water in oil (W-O). In every case there is present a third substance, the emulsification agent, which stabilizes the emulsions and determines the type. As a very general statement it may be said that, in dilute systems, the O-W emulsion resembles hydrophobic sols as regards stability, while the W-O systems show similarity in behavior to fogs and smokes.

The formation of an emulsion requires the development of extensive new surface between the two liquids. There is a wide variety of technical and laboratory instruments used for the purpose. They are the agitators, churns, whisks, colloid mills, homogenizers, and ultrasonic waves which disperse the internal phase. The extent of dispersion may be determined by an examination of the particle size and particle size distribution (size-frequency) in the system, using microscopic, photomicroscopic, or sedimentation methods. Many emulsions contain droplets of relatively large diameters when compared to those usually recognized as being within the region of size for colloidal particles, but emulsions in general are considered as colloidal systems because the emulsification agent, often polymolecular, forms surface film protective coating to stabilize them.

Perhaps the earliest explanation of the formation of an emulsion is the surface tension theory of Quincke,<sup>2</sup> Donnan,<sup>3</sup> and Bancroft,<sup>4</sup> in which the emulsification agent is described as lowering the interfacial tension between the two

<sup>1</sup> General references are: Berkman and Egloff, *Emulsions and Foams* (New York: Reinhold Publishing Co., 1941); Clayton, *The Theory of Emulsions and their Technical Applications* (4th ed.; Philadelphia: Blakiston Co., 1943); Lange, *Technik der Emulsionen* (Berlin: Julius Springer, 1929); Lewis, Squires, and Broughton, *Industrial Chemistry of Colloidal and Amorphous Materials* (New York: The Macmillan Co., 1942); du Noüy, *Surface Equilibria of Biological and Organic Colloids* (New York: Reinhold Publishing Co., 1926); Travis, *Mechanochemistry and the Colloid Mill* (New York: Chem. Catalog Co., 1928); Symposium: *Emulsion Technology* (2d ed.; New York: Chemical Publishing Co., 1946); *Wetting and Detergency* (2d ed.; New York: Chemical Publishing Co., 1939).

<sup>2</sup> Quincke, *Ann. Physik*, 35, 571 (1888).

<sup>3</sup> Donnan, *Z. physik. Chem.*, 31, 42 (1899); Donnan and Potts, *Kolloid-Z.*, 7, 208 (1910).

<sup>4</sup> Bancroft, *J. Phys. Chem.*, 17, 501 (1913); Bancroft and Tucker, *ibid.*, 31, 1681 (1927).

liquids and is thereby concentrated at the interface. The liquid with lower surface tension or the liquid which better wets the emulsification agent becomes the dispersion medium.

Another theory, known by the name "oriented-wedge" and described almost simultaneously by Harkins <sup>5</sup> and by Hildebrand, <sup>6</sup> suggests that the stabilizing agent, a long chain-paraffin salt concentrates in the interface in such fashion that the inorganic part is dissolved in the water and the organic residue is enveloped in the organic liquid. With dimensions of anion and cation relatively well known it becomes possible to calculate droplet size for a given emulsification agent, but on exact study Stamm and Kraemer <sup>7</sup> have failed to find agreement between observed and calculated particle size. The theory seems to assume too ideal a structure for the paraffin chain salt at the interface.

Modifications of these general ideas have appeared from time to time. As an example we mention a recent report of Schulman and Cockbain, <sup>8</sup> who suggest that for the formation of a stable emulsion it is necessary to form in the surface of the droplet a complex film of at least two components, one soluble and anchored in the oil, and the other in water. If the two agents have suitable shapes, dimensions and attractive forces between them, a stable film will result, and if the interfacial tension between the two liquids is greatly reduced, the resulting emulsion is permanent. These investigators, as well as many others, have considered the problem of phase inversion.

The type of an emulsion may be determined from the properties of the external phase. An emulsion is freely miscible with its dispersion medium. Thus, an O-W emulsion can be diluted with water, but a W-O emulsion will rise to the surface of water. The tests are usually carried out on a microscope slide. Electrical conductivity, dye solubility and other tests have been also proposed.

There are several effective means of breaking an emulsion. The emulsification agent may be changed in character by the addition of a reagent which reacts with it, or its influence may be destroyed by the addition of the proper amount of an agent which normally produces the opposite type of emulsion. Many emulsions can be broken by freezing or by simple agitation. The water may be removed from some W-O oil field emulsions by the passage through the system of a high voltage alternating current, analogous to Cottrell precipitation.

(75) **Aerosols:** <sup>1</sup> Three types of aerosol, i.e., dispersions of finely divided solids and liquids in gases, are to be distinguished; the dusts and smokes in which the suspended particles are nonvolatile, and the fogs in which the particles are volatile. The properties of these systems are greatly different from the ones which have been considered in connection with the liquid sols. Smokes

<sup>5</sup> Harkins, Davies, and Clark, *J. Am. Chem. Soc.*, **39**, 541 (1917).

<sup>6</sup> Finkle, Draper, and Hildebrand, *ibid.*, **45**, 2780 (1923).

<sup>7</sup> *J. Phys. Chem.*, **30**, 992 (1926).

<sup>8</sup> *Trans. Faraday Soc.*, **36**, 651, 661 (1940).

<sup>1</sup> The papers presented at the Symposium on Aerosols, at the 113th National Meeting of the American Chemical Society, Chicago, 1948, are published in *Chem. Rev.*, **44**, 245-417 (1949).

are usually formed as part of a chemical reaction such as combustion. A dust results from the dispersion of solid material. On the other hand a fog or cloud is formed in a condensation process in which dust particles or free ions may act as nuclei for the droplet formation.

*Clouds:* When consideration is given to the formation of liquid droplets in a gas, we must recognize that the vapor pressure of the drop is a function of its radius. Since the vapor pressure of a small drop is higher than that over a plane surface of the liquid there cannot be any appreciable formation of drops until the concentration of the vapor is raised to approach the vapor pressure of the small drops.

In taking a small amount of liquid from the plane surface and transferring it to a drop, a certain amount of energy,  $2\gamma/\rho_l r$ , is expended against the surface tension. Here  $r$  is the radius of the drop,  $\gamma$  is the surface tension, and  $\rho_l$  is the density of the liquid. If the same amount of liquid is now distilled from the drop, where the vapor pressure is  $p_r$ , to the plane surface, where the vapor pressure is  $p$ , the gain in energy is  $(RT/M) \ln p_r/p$ , where  $M$  is the molecular weight. Since the two amounts of energy are equal, we have

$$\ln \frac{p_r}{p} = \frac{2\gamma}{\rho_l r} \frac{M}{RT} \quad (75.1)$$

If  $p_r/p$  is not greatly different from unity, it follows, as an approximation, that

$$p_r = p + \frac{2\gamma}{\rho_l r} \frac{Mp}{RT} = p + \frac{2\gamma}{\rho_l r} \rho_v \quad (75.2)$$

Here  $\rho_v$  is the density of the vapor. This equation cannot be assumed to hold below a radius of  $10^{-7}$  (about 133 molecules) because (1) as the number of molecules decreases, the concept of a flat surface under uniform tension must fail and (2) it is impossible to speak of a saturation pressure when the equilibrium pressure depends upon the concentration of clusters present as it obviously does in the limit when only bimolecular clusters are present.<sup>2</sup>

The situation is quite different if in the mixture of air and water vapor, for example, there are present dust particles or products from chemical or photochemical processes which may act as condensation nuclei. Thomson<sup>3</sup> has developed the theory for the case in which the nuclei for condensation are electrically charged. The formula for the increase in vapor pressure in the form of (75.1), now becomes

$$\ln \frac{p_r}{p} = \frac{M}{RT\rho_l} \left( \frac{2\gamma}{r} - \frac{e^2}{8\pi r^4} \right) \quad (75.3)$$

where  $e$  is the charge carried by the drop.

<sup>2</sup> Rodebush, *Chem. Rev.*, **44**, 269 (1949).

<sup>3</sup> *Conduction of Electricity through Gases* (London: Cambridge University Press, 1903).



The relation between  $p_r/p$  and  $r$  for uncharged and charged droplets is shown in Fig. 42, A and B, respectively. It indicates that in the case of a monovalent gas ion condensation should begin at a supersaturation of approximately 4.2.

Wilson <sup>4</sup> has studied the condensation process upon cooling by adiabatic expansion. From the change in volume it is possible to calculate the drop in temperature, and, therefore, the degree of supersaturation. It was found that condensation takes place on negative gas ions in the region of supersaturation of 4.2 to 5.0, and on the positive ions at the supersaturation degrees 5.8 to 6.8. The condensate is rain-like in character because ions are not numerous in ordinary air, so there are few nuclei to develop. At degrees of supersaturation higher than 8 the number of drops rises sharply and the appearance of the condensate changes to that of a dense white cloud.

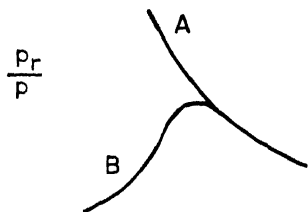


FIG. 42. Relative Vapor Pressures of Charged (B) and Uncharged (A) Liquid Droplets as a Function of Radius.

In their studies of the production of ice crystals in a cloud of supercooled water droplets, Schaefer <sup>5</sup> and Langmuir found that at  $-10$  to  $-20^{\circ}\text{C}$  various types of dust particles such as graphite, sulfur, talc, volcanic dust, and silicates failed to initiate crystallization of the supercooled cloud. However, solid carbon dioxide caused the immediate formation of crystals, and it was ascertained that in order to obtain spontaneous transformation from water to ice it was necessary to

use temperatures of  $-35^{\circ}\text{C}$  or lower. By scattering small fragments of dry ice in supercooled clouds from a plane Langmuir and Schaefer have shown that under the proper conditions the cloud is converted into ice crystals.

Silver iodide <sup>6</sup> particles also have been found to serve as nuclei for the formation of ice crystals. It is believed that silver iodide serves as a very effective nucleus because it very closely resembles ice in crystal structure and the dimensions of the unit cell are the same as water to within 1 per cent.

When a liquid is sprayed into a gas the droplets become charged. Alternatively, when neutral clouds are exposed to radioactive substances positive and negative ions are formed. Use of this latter fact may be made for the estimation of droplet size. In an electrical field the force imparted to the particle of charge  $e$  is  $Xe$ , where  $X$  is the field strength. This force is opposed by the frictional resistance force of the medium of viscosity  $\eta$ , and for steady rate of fall  $v$ , we have

$$v = \frac{Xe}{6\pi\eta r} \quad (75.4)$$

<sup>4</sup> *Phil. Trans. Roy. Soc., A* 192, 403 (1899); *Proc. Roy. Soc., A* 87, 277 (1912).

<sup>5</sup> *Science*, 104, 457 (1946); *Chem. Rev.*, 44, 291 (1949).

<sup>6</sup> Vonnegut, *J. Appl. Phys.*, 18, 593 (1947); *Chem. Rev.*, 44, 277 (1949).

Another method for the estimation of droplet size depends upon another use of Stokes's law in which the force of sedimentation is balanced by the frictional resistance to movement, and

$$\frac{2r^2(\rho - \rho_0)g}{9\eta} \quad (75.5)$$

where the symbols have their usual significance. These formulae are subject to certain limitations and corrections; they then form the basis for the classical Millikan oil-drop experiments in which the charge on the electron was precisely determined.

*Smokes and Dusts:* Although smokes and dusts are alike in that they are composed of solid particles suspended in a gas, the mode of formation is often sharply different. Smokes are usually formed as a result of a condensation process, but dusts originate in dispersion mechanisms. Like the fogs, they are much less stable systems than the hydrosols. But they are of great industrial significance, often nuisance, because of stack losses, dust explosions, air pollution, etc., and are thus deserving of more intensified study.

In general, dusts consist of larger particles and settle more rapidly than smokes. The actual number concentration of particles is usually low, but on account of the relatively large particle sizes they reflect light and show a high optical density and Tyndall phenomenon. This latter fact is made use of in the determination of concentration in the aerosol. Among others, Tolman and Vliet,<sup>7</sup> LaMer and Sinclair,<sup>8</sup> and Gucker, Pickard, and O'Konski<sup>9</sup> have studied the intensity of the light scattered at right angles and at small forward angles to the Tyndall beam in its relation to sol concentration.

In the method developed by Gucker and co-workers a fine stream of the aerosol, protected by a flowing sheath of pure air, passes through a spot under intense dark-field illumination and scatters flashes of light forward upon a photo-sensitive cell. Each particle of about 0.6 micron or more in diameter causes an electrical pulse which is sufficiently large, after suitable amplification to operate a mechanical counter.

One well-known instrument used in connection with the coagulation of smokes and dusts is the precipitator of Cottrell.<sup>10</sup> In principle, with a needle-point electrode and a plate electrode connected to the two sides of a high-potential DC line, the space between the electrodes becomes charged with electricity of the same sign as the needle point, and an insulated body brought

<sup>7</sup> *J. Am. Chem. Soc.*, **41**, 297 (1919).

<sup>8</sup> Sinclair and LaMer, *Chem. Rev.*, **44**, 245 (1949).

<sup>9</sup> *J. Am. Chem. Soc.*, **69**, 429 (1947); Gucker and O'Konski, *Chem. Rev.*, **44**, 373 (1949).

<sup>10</sup> *Ind. Eng. Chem.*, **11**, 147 (1919).

into this space acquires a charge of the same sign. A suspended particle will thus move to the plate and be discharged and collected.<sup>11</sup>

<sup>11</sup> (*Footnote added in proof.*) The manuscript for this section was submitted to the Editors in September, 1947. In July, 1949, certain additions were made, and some new references have been added in proof.

J.W.W. and R.A.A.

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